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# Studies in Vapor Pressure

## A DISSERTATION

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# STUDIES IN VAPOR PRESSURE: I. A STATIC METHOD FOR DETERMINING THE VAPOR PRESSURES OF SOLIDS AND LIQUIDS.[1]

This paper consists of five sections dealing, respectively, with:

(1) The sources of error of a more general character involved in vapor pressure measurement.

(2) A critical résumé of the characteristics of the older methods, with particular reference to the individual sources of error in each.

(3) A description of the present apparatus.

(4) A criticism of this apparatus, in relation to the various sources of error.

(5) A set of measurements of the vapor pressures of water, made with a view to testing the efficiency of the apparatus.

The apparatus was applied in a redetermination of the vapor pressure of mercury, and in a quantitative study of the chemical constitution of calomel vapor, which will be described in separate papers.

## Section 1. General Sources of Error Involved in Vapor Pressure Measurement.

A critical study of the very voluminous literature of vapor pressures reveals the fact that, where two or more independent series of values for the same substance are in existence, inconsistency is the rule and substantial quantitative agreement throughout two comparable series the exception. The differences range from a few tenths of a millimeter

[1] This paper, and the two following, were read at the Boston meeting of the Society, on Dec. 30, 1909.

to several hundred millimeters.[1] In view of this discordance, which affects also our own results when they are compared with those of others, some space must be taken to discuss the general sources of error in the measurement of vapor pressure and to give some account of the older methods. The aim of this discussion is to attempt to indicate the precise conditions that must be met if these chief sources of error are to be avoided. When the sources of error have thus been defined, it is possible to show how far the method described in this paper meets the required conditions, and how far confidence may be placed in the experimental results secured by its means.

The sources of errors that are common to most methods of vapor pressure determination may, perhaps, be best discussed under the three heads of temperature, pressure, and impurity of material:

**Temperature.**—(*1*) *Steadiness and Equal Distribution.*—When the condensing vapor from a liquid boiling in a flask is used to maintain a steady temperature, the vapor, at first inevitably superheated, is expected to cool itself to the boiling point by radiation and by giving up heat to the bodies that it encounters. If the latter are too thoroughly jacketed, they may not lose the heat sufficiently fast to cool to the boiling point the vapor in the neighborhood of the thermometer. Errors, therefore, arise when the boiling is rapid, or when a sand bath or other large radiating surface is used as a source of heat. With inadequate jacketing, on the other hand, the latent heat of the vapor may be insufficient to raise the temperature of the heated bodies to the boiling point. This is a common experience, for example, in determining the sulphur boiling point of a platinum thermometer. In this connection it has not always been borne in mind that the latent heat of evaporation of water is exceptionally high, that of other liquids having, at their boiling points, only a fraction of the value for water. Again, when the liquid is boiled under reduced pressure,[2] the mass of vapor condensing is necessarily smaller, and its heating power, in virtue of latent heat, much less. It will be seen that, for a steam jacket, a much greater latitude in strength of heating (*e. g.*, of flame-height) is possible than for other jacketing vapors.

Liquid baths, having a large volume and therefore a large heat capacity, have generally been found satisfactory in maintaining steady temperatures whenever the stirring was adequate (see Section 3, below), which, however, has not always been the case. Air baths, on account of ther small heat capacity, are far inferior,[3] and when employed have frequently not been stirred at all.

[1] See Landolt and Börnstein's, or any similar set of tables.

[2] As in Ramsay and Young's method of securing any desired temperature from 0° to 360°, by use of eight liquids (*J. Chem. Soc.*, **47**, 640; **55**, 483).

[3] See, *e. g.*, this series, No. III, following.

(2) *Accurate Determination of Actual Temperature.*—Explicit statements of the method of standardization of the thermometers used and of the degree of probable accuracy in the measurement of temperature are frequently wanting. In mercurial thermometry, it may be mentioned, the correction for external pressure upon the bulb is very uniformly omitted (see Section 2, below); too much faith is placed in an arithmetical correction for "exposed thread;" and readings to tenths above 300° are treated with too much respect.

(3) *Scale of Temperature.*—In few cases is the scale specified or, apparently, considered. Since even so low as 200° the difference between the constant-pressure air scale and the thermodynamic scale is of the order of 0.1° (corresponding to a pressure difference of several mm.), and at 450° the difference is nearly 0.5°, it would appear that many refinements in measuring or calculating pressures to single millimeters, not to speak of tenths, hundredths, and even thousandths of a mm. that are found in the literature, are really superfluous.

As a sample of vapor pressure thermometry, similar to dozens that might be cited, the determination of the vapor pressures of iodine by E. Wiedemann[1] may be mentioned. At 180°, for example, he found the value 687.2 mm. Since he says nothing about the style of the thermometer, about corrections, or about the scale of temperature referred to, two of these figures in the pressure are without significance. It is not remarkable, therefore, that the value is 25 mm. (corresponding to nearly 1.5°) divergent from that of Ramsay and Young,[2] and that his results add absolutely nothing to our previous knowledge.

**Pressure.** — The straightforward reduction of gage and barometer readings to mm. of mercury at 0° is not always stated to have been performed. Correction is made for the varying value of the gravity constant (*g*) only in very exceptional cases. Yet, in Chicago, a place not very elevated, and not far from 45° N. L., this correction amounts to 0.25 mm. per 760 mm., and in laboratories in London the value is about 0.5 mm. per atmosphere. This correction, therefore, usually considerably exceeds the error involved in the mere reading of the gage.

**Impurity.**—In he matter of purifying the crude material for the purposes of vapor pressure measurement, the physicist is usually admittedly at a disadvantage. But here even the chemist may be found somewhat unintelligently distilling "nine times" or freezing out or recrystallizing "fifteen times", with no guarantee that any increase of purity is being attained. How real is the necessity for purification may be judged from the statement of Tammann[3] that 0.01 per cent. of alcohol in benzene

[1] *Ber. physik. Ges.*, **3**, 159 (1905).
[2] *J. Chem. Soc.*, **49**, 453 (1886).
[3] *Ann. Physik*, [3] **32**, 683 (1887).

raised the vapor pressure of the latter, near the boiling point, by 12 mm.

A somewhat different class of impurity is met with in the moisture, oxygen, nitrogen and carbon dioxide dissolved in liquids or adhering to solid substances. Such impurities form undoubtedly a most constant and elusive source of error. The seriousness of the error due to this cause, however, varies much with the particular method employed. Attention may, perhaps, here be called to a fact which seems to be very generally overlooked, namely, that gases are, as a rule, much more soluble in other liquids than in water, and therefore, in general, have in other liquids more effective vapor pressure, and are less quickly and easily removed by boiling and other precautions than in the case of water. In the following table[1] the solubilities of three common gases are stated as volumes of gas held in solution by one volume of various liquids under ordinary conditions.

| Liquid. | Carbon dioxide, 25°. | Nitrogen, 25°. | Oxygen, 20°. |
|---|---|---|---|
| Water | 0.83 | 0.016 | 0.028 |
| Carbon disulphide | 0.87 | 0.059 | ... |
| Benzene | 2.43 | 0.116 | ... |
| Chloroform | 3.43 | 0.135 | ... |
| Methyl alcohol | 3.84 | 0.142 | ... |
| Acetic acid | 4.68 | 0.119 | ... |
| Amyl acetate | 4.12 | 0.173 | ... |
| Acetone | 6.29 | 0.146 | ... |
| Alcohol | .... | ... | 0.284 |
| Petroleum | 1.17 (20°) | 0.117 (20°) | 0.202 |

It may be pointed out in this connection that there is, probably partly for this reason, far less inconsistency in vapor pressure measurements of different observers in the case of water than in that of any other liquid. In many vapor pressure determinations there is no record of even an attempt to remove gases by preliminary boiling. Other observers boil for "two minutes" or for "some time." Not one of the widely used static methods admits of repetition of the boiling-out process till constant results are obtained, and thus the only sure proof of the effectiveness of the attempt to remove impurities is lacking[2] (see Section 2).

## Section 2. The Older Methods.

Only certain methods will be here considered which are applicable over wide ranges of temperature, no mention being made of the tensi-

[1] These figures are mainly from Just, *Z. physik. Chem.*, **37**, 354.

[2] A re-opening of the apparatus and repetition of the boiling out, or some equivalent process, so far as we have noticed, is mentioned only as follows: Ramsay and Young, *Phil. Trans.*, **177**, 91 (1888), part of the observations with a single substance ($NH_4Cl$) only. Lescoeur, *Ann. chim. phys.*, [6] **16**, 389 (1889). Beckmann, *Z. physik. Chem.*, **4**, 534; Raoult, *Ann. chim. phys.*, [6] **20**, 301 (1890), liquid boiled, but not the mercury; method not applicable above 1 atm. Vanstone, *J. Chem. Soc.*, **97**, 429 (1910).

metric, gas-current, dew-point, and other methods of limited range. Regnault's classification of methods into "static" and "dynamic" may be followed.

**Static Methods.**—As representing a large class of static methods, may be taken that form in which the substance is introduced into the Torricellian vacuum of a jacketed barometer tube. A special temperature error incident to this method arises from the difficulty of adequately stirring a tall bath of liquid, such as those used by several of the French investigators. The difficulties when the vapor of a boiling liquid is used for heating have been discussed already. The pressure measurement is naturally uncertain in those cases, which are by far the majority, where every part of the mercury column is not held at the same temperature as the vapor chamber.

But the chief source of error in this form of the static method lies in the impurity of the substance. In the first place, mercury vapor may be present as an impurity. We find Ramsay and Young at one time applying the correction for complete saturation of the vapor chamber with mercury vapor, while, under other circumstances, Young assumes the entire absence of mercury vapor. If the correction be made, its value, at least above 280°, has hitherto been uncertain. Far more serious, however, is the uncertainty as to the inclusion with the substance of gases and moisture from the air, absorbed or dissolved in the solid or liquid, or adhering to the walls of the tube. Some observers attempt merely so to fill the tube with mercury that visible bubbles are absent. In such cases large amounts of absorbed gases must be liberated when the heating begins. Even with thorough boiling out, visible bubbles (not to speak of absorbed and invisible gases) may remain.[1] To remove gaseous impurities, the most careful workers, for example, Ramsay and Young,[2] boil, first the mercury and then the substance, in the barometer tube before inverting the latter. But even in such cases, save for the few exceptions mentioned in Section 1, a repetition of the boiling out, to test the success of the procedure, has never been attempted. What would the chemist say of a gravimetric method in which heating to constant weight played no part? The adhesion of the liquid to the top of the barometer tube, frequently cited, is, no doubt, evidence against the presence of free "air," but hardly excludes the presence of dissolved and absorbed "air." It may be questioned, also, whether obtaining almost identical pressures with varying volumes of liquid and vapor is

[1] Tammann, in a piece of work on the effects of small amounts of impurities (*l. c.*), boiled out thoroughly, and remarks that after this treatment there was "usually no air-bubble" in the tube.

[2] *Phil. Trans.*, **175**, 461 (1884). Young, *Stoichiometry*, 131.

a proof of the absence of foreign matter.[1] At all events, Ramsay and Young's method, the results of which usually were satisfactory when judged by those two criteria, happened to be tested in a different way in a single instance.[2] This tube was filled with mercury, which was thoroughly boiled in the tube as usual. Without the introduction of any substance, however, this tube was heated at 280.1°, as for a determination. When the tube had cooled, a permanent gas was found to have accumulated. Calculation showed that, while the tube was at 280.1°, this gas must have exercised a partial pressure of 2.9 mm. A second heating, if attempted, might have resulted in an increase in the amount of this gas. If a substance had been added, the amount of foreign gas could only have been still further augmented, so there is no assurance that these two tests are sensitive within $\pm 3$–5 mm. of foreign gas. Ramsay and Young's results are probably not subject to a systematic error, on account of filling, of such dimensions as this, but their exactness is due rather to the skill of the experimenters than to an inevitable accuracy inherent in the method.

The U-form apparatus, used by some investigators instead of a straight barometer tube, and applicable especially to pressures over one atmosphere, is open to very similar sources of error. Of quite another type is the static method in which pressure is measured by means of the Ladenburg spiral gage.[3] Here again, however, what is chiefly to be desired is a procedure which will permit of repetition of the boiling-out process until constant results are obtained.

If an individual observer with a constant personal equation has difficulty in duplicating results by the static method, it is not to be wondered at that different observers differ among themselves. Take, for example, the vapor pressures of acetic acid at 100°, all as measured by the static method: Landolt 408.5 mm., Ramsay and Young 417 mm., Wüllner 473 mm.; those of butyric acid at 20.3°: Landolt 7.3 mm., Ramsay and Young 0.35 mm.

Not the least of the objections to the static method is the almost unbearable laboriousness of work which attempts to be accurate. Schmidt,[4] after enumerating its difficulties, including one not noted by other observers, namely that a number of barometer tubes had to be rejected before one was found in which the pressures with small amounts of vapor were not larger than with greater amounts, adds: "The static method

[1] Young, *J. Chem. Soc.*, **55**, 486 (1889). Abnormalities when the proportion of the liquid phase is *exceedingly minute* have indeed been observed (Wüllner and Grotian, *Ann. Physik*, [3] **11**, 545; see also Ramsay and Young, *Phil. Trans.*, **183**, 107).

[2] *Phil. Trans.*, **177**, 87 (1886).

[3] *Z. physik. Chem.*, **61**, 458; also *Ibid.*, **68**, 129. See No. III of this series.

[4] *Z. physik. Chem.*, **8**, 629.

has so many disadvantages, when compared with the dynamic, that I can only warn [observers] not to use it."

**Dynamic Methods.**—A simple form of the dynamic method consists in using a thermometer immersed in the vapor rising from a liquid boiling under various known pressures. So, for example, Regnault obtained his vapor pressure curve for sulphur, and Holborn and Henning their data for water. It is plain that such a method escapes the errors due to gaseous impurity, whether adhering or dissolved, and herein lies its chief advantage over the static methods. If a reflux condenser be employed, moisture and condensable volatil impurities do not escape; while if the vapor is condensed in another vessel, the less volatil impurities become concentrated in the residual liquid. In either case, if the current of vapor streaming into the condenser be a rapid one, the pressure within the flask is commonly slightly higher than the pressure at the distant end of the condenser with which the manometer is connected. Irregular boiling may cause large errors, and is difficult to prevent. Use of a stream of air entering through a capillary vitiates the results,[1] so far as their value as vapor pressure measurements is concerned. Schmidt[2] avoids bumping by placing a pad of cotton, saturated with the liquid, in the bottom of the flask. Regnault's difficulties and results in the case of mercury will be referred to later.[3]

Ramsay and Young sought to overcome the bumping and superheating difficulties, as well as the disadvantage of the large quantity of material required, and to avoid the need of a bath which could keep the apparatus at a constant and known temperature, by means of their well-known method.[4] In this, the liquid is allowed to trickle on to cotton enveloping the thermometer bulb. This bulb is situated in a flask surrounded by a bath, the temperature of which need not be constant or definitly known, but must be at least 20° higher than that shown by the thermometer. When the pressure, which is read by means of a manometer in connection with the flask, is altered, the temperature as shown by the thermometer changes spontaneously to correspond. It will be seen that the thermometer readings are subject to the correction for the "compression coefficient," as noted by us in a former paper,[5] although

[1] For discussion of this, and of other sources of error, see *J. Am. Chem. Soc.*, **32**, 911.

[2] *Z. physik. Chem.*, **7**, 440; **8**, 628.

[3] See No. II of this series, following.

[4] *Phil. Trans.*, **175**, 37 (1884); *J. Chem. Soc.*, **47**, 42; Young, *Stoichiometry*, 140 Ostwald-Luther, [2] 177.

[5] *J. Am. Chem. Soc.*, **32**, 905. The purpose of this paper, on "A Common Thermometric Error in the Determination of Boiling Points under Reduced Pressure," seems not to have been made sufficiently clear in the paper itself. Physicists have long been familiar with the "compression coefficient," although even some of them ignore

this correction, amounting in certain cases to nearly 0.2°, is not mentioned in any of the published descriptions of the apparatus, or applied so far as we have seen, with a single exception, on any of the numerous occasions on which the method has been employed.

The error due to impurity is here to be looked for from the presence of air in the cotton wool and also, more especially, dissolved in the liquid. Fresh supplies of liquid with its dissolved "air" are constantly being introduced, nullifying any possibility of permanent expulsion by boiling out. The chief advantage of the simple dynamic method is thus lost, and the chief disadvantage of the static method is re-introduced. Should the liquid have acquired a non-volatil impurity, or contain by heredity an impurity less volatil than itself, it is plain that such impurity must gradually become more and more concentrated in the cotton surrounding the thermometer bulb. The method is not applicable to pressures much greater than atmospheric, or to liquids (*e. g.*, mercury) which do not wet cotton, and is of questionable value for solids.[1]

### Section 3. The Apparatus.

The special feature of the submerged-bulblet vapor pressure apparatus, already described,[2] consists in the facility with which, using only a minute amount of the substance, the expulsion of dissolved and adhering impurities may be continued until constant values for the vapor pressure are secured. This important feature is precisely the one most conspicuously required to give trustworthiness to the static method and, as we have seen, most conspicuously lacking in the standard forms of apparatus working on the static principle. Now, while the bulblet method was being reduced to suitable form, we perceived that a modification of the apparatus would convert it into a static instrument. This static apparatus retained the advantages of the important feature referred to without loss of ease of manipulation, and possessed also several additional advantages over the regular static forms of apparatus. The simple bulblet was first changed by using a wider tube, instead of the capillary, and bending the lower end of the tube upwards. The whole had thus the form of a C, and an enlargement of the open end furnished a cup into which a confining liquid could be temporarily driven during the boiling-out process. The C-formed apparatus was tied to the thermometer, just as was the simple bulblet. To allow further liberty in

it in vapor pressure work. The paper dealt with the types of thermometers commonly employed by chemists, and with the considerable dilatations occurring when large intervals of pressure are concerned. The effects cannot be ignored in vacuum distillation and in vapor pressure determinations by the cotton-jacketed-thermometer method, for example, both of which are operations much used by chemists, and not hitherto associated in their minds with the necessity of employing this correction.

[1] See No. III of this series.

[2] *J. Am. Chem. Soc.*, **32**, 907.

the choice of a confining fluid, the open limb was next lengthened so as to extend above the surface of the bath. After a series of minor changes, the form described below was finally adopted.

It is necessary to describe the apparatus and the corrections used in minute detail, as only thus can the exact conditions be understood, and only thus can the data secured retain their value if, for example, sources of error which have escaped attention should subsequently be discovered.

**The Isoteniscope, Bath, and Stirrer.**—The substance is placed in the spherical bulb, which is about 20 mm. in diameter (Fig. 1). The confining liquid occupies the lower half of the U-tube, which is 30–35 mm. in height. The small bulbs on each limb of the U-tube prevent the ascent of the confining liquid (by suction) into the bulb or the vertical tube. For the sake of compactness, the spherical bulb is placed behind the U-tube, and not in the same plane with it as shown (for clearness) in the figure, the purpose of the apparatus being to show when two pressures have become equal, the arrangement may be called an *isoteniscope*. The present form, to distinguish it from a different one to be described in a later paper, may be called the *static isoteniscope*. A two-liter beaker of tall shape forms the bath. The vertical tube of the isoteniscope is about 24 cm. long, so that the rubber connection is sufficiently far above the heated bath-liquid.

Fig. 1.

When the substance being studied is a liquid, the lower part of the U-tube is charged with *this liquid itself*. When the substance thus acts as its own confining liquid, it has the great advantage over mercury that its specific gravity is usually small. Hence, when the levels in both limbs of the U-tube appear to the eye to be identical, the error, when converted into mercury height, is negligible.

It is only when the vapor pressure of a non-fusing solid is being determined that the question of choosing a confining liquid comes up. The conditions to be fulfilled are that the confining liquid shall not have an appreciable vapor pressure of its own at the temperatures to be employed, and that the vapor of the substance shall not dissolve in it. A liquid which interacts chemically with the vapor of the substance should be avoided, especially if a gas is produced. But, as will be seen in the paper on the constitution of calomel vapor, a slow chemical action involving no gas production is not prohibitory. Among the suitable substances are mercury and melted paraffin at the lower temperatures, and fusible alloys or a molten salt or mixture of salts at high temperatures. In the

case of solids, it is necessary to charge the bulb before fusing it to the U-tube.

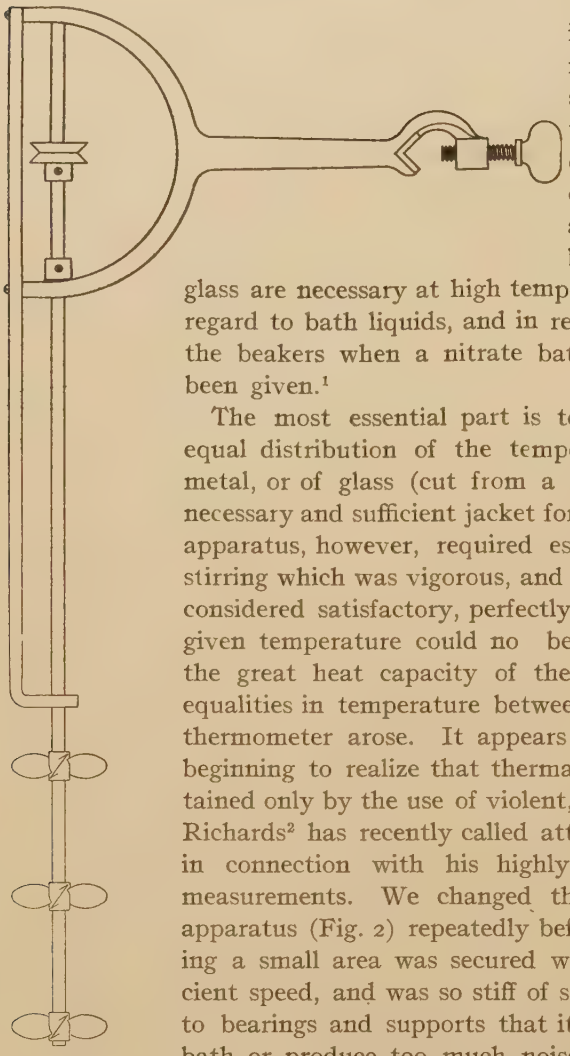

Fig. 2.

To permit sufficient immersion of the thermometer (platinum resistance, or mercury) in the bath-liquid, beakers over 23 cm. high and 11 cm. wide are used, and are filled almost to the brim. Beakers of Jena glass are necessary at high temperatures. The details in regard to bath liquids, and in regard to the handling of the beakers when a nitrate bath is used, have already been given.[1]

The most essential part is to secure steadiness and equal distribution of the temperature. A cylinder of metal, or of glass (cut from a broken beaker), forms a necessary and sufficient jacket for the bath. The stirring apparatus, however, required especial attention. With stirring which was vigorous, and of the nature ordinarily considered satisfactory, perfectly constant pressures at a given temperature could no be obtained. In spite of the great heat capacity of the bath-liquid, slight inequalities in temperature between the substance and the thermometer arose. It appears that chemists are only beginning to realize that thermal equilibrium can be obtained only by the use of violent, almost riotous stirring. Richards[2] has recently called attention to the same fact, in connection with his highly exact thermochemical measurements. We changed the form of our stirring apparatus (Fig. 2) repeatedly before a structure occupying a small area was secured which rotated with sufficient speed, and was so stiff of stem and so massive as to bearings and supports that it did not "whip" in the bath or produce too much noise.[3] When these conditions had been met, constant results, even with a resist-

[1] *J. Am. Chem. Soc.*, **32**, 899.

[2] *Ibid.*, **31**, 1280 (1909).

[3] The stirrer (Fig. 2) was made from an ordinary retort-stand ring. The rod (3 mm. in diameter), driven rapidly by an electric motor, rotates in two holes bored in the ring, and is supported by a stout strip of brass (seen edgewise) which extends down almost to the first vane. The length from the lower side of the ring to the lowest vane is 28 cm. The vanes are in sets of three, each set 25 mm. in diameter.

ance thermometer giving a large galvanometer deflection for one hundredth of a degree, were easily secured, where before they had seemed unattainable.

It is important to place the stirrer so that it may communicate some of its vibration to the substance (if a liquid) in the bulb. The resulting, constant agitation promotes the liberation of the vapor. It also prevents the limitation of the evaporation to the mere surface layer, a condition which would delay or prevent the complete elimination of dissolved gases.

By use of transparent quartz for the vaporizing vessel, and a quartz beaker, there is no reason why this method should not give exact determinations of vapor pressures and of dissociation pressures up to the softening point of quartz. Vapor pressures have not yet been measured accurately at such temperatures and, for dissociation pressures, the combination of a platinum heating chamber fused to a U-tube of glass, to render the confining liquid visible,[1] has several disadvantages.

**The Platinum Resistance Thermometer.**—While a mercury thermometer may be used, the platinum resistance thermometer is, of course, a more exact and trustworthy instrument. Quite apart from this, however, the latter has a special advantage in work of this kind, where the complete expulsion of foreign matter is ascertained by repeated observations, made at exactly the same temperature. After a second boiling out and equalization of the pressures, the temperature of the bath itself can be readjusted until the spot of light occupies its precise former position. Thus, while the actual temperature may not be known with a greater accuracy than $\pm 0.1°$ or $\pm 0.01°$, according to the precautions taken, this readjustment of the bath temperature may very easily be made with an error much smaller than these.

The platinum resistance thermometer employed was of the form devised by Haagen.[2] In this form, the resistance wire is wound on a 6 cm. length of quartz tube, of diameter somewhat over 1 mm., which is then inserted into a very slightly wider quartz tube. The outer tube is then fused on to the inner one, thus embedding the resistance wire in quartz. The "bulb" so prepared is fused to a suitable length (24 cm.) of wider quartz tubing which carries the platinum and silver leads. There are no compensation leads.

For measuring resistance a Wheatstone bridge arrangement was used, with an arm ratio of 10 to 1. The box resistances, of manganin, were calibrated, and the appropriate correction applied to all measurements made. The largest error of any of the single coils employed was 2.6 parts in 10,000. The coils were not maintained at constant temperature, but, in order that the temperature correction applied might be as small

[1] John Johnston, *Z. physik. Chem.*, **62**, 330 (1908).

[2] *Z. angew. Chem.*, **20**, 565.

as possible, the temperature of the coils was kept close to that which they possessed when the fixed points were determined. The resistance of the thermometer was about 50 ohms at 0°. The measuring current varied from 3 milli-amperes at 0° to 1.2 at 445°. No correction for heating by the measuring current was required when the thermometer was immersed in water, fused nitrates, steam at 100°, or sulphur vapor at 445°. A small correction was necessary only when moistened ice, with its badly conducting, interstitial air spaces, surrounded the thermometer bulb. The sensitiveness of the galvanometer was such that a movement of the light spot of 1 cm. on the scale corresponded to 0.04° at 0° and to 0.08° at 445°. The fixed points used were the freezing point of water, the boiling point of water and the boiling point of sulphur. The boiling point of sulphur was assumed, in accord with Holborn and Henning,[1] at 445°. Its true value may lie closer to 444.9° on the thermodynamic scale,[2] but, as this datum is liable to be changed by future observations, it was thought better to adopt the rounder number. Obtaining the ice point and the water boiling point presents little difficulty, if the usual precautions are observed. As is well known, however, the boiling point of sulphur found varies considerably with the size of the apparatus and the screening, etc., adopted.[3] We employed a gas-heated boiling tube of thin brass of 5.5 cm. diameter and 47 cm. length, jacketed by a thickness of 5–6 cm. of asbestos packing. The bulb was protected by a cone of asbestos paper, closed below, whose base was situated 10–12 cm. above the surface of the boiling sulphur and whose apex was 20 cm. below the level of condensation. We were careful to employ the roll sulphur of commerce, and used a depth of about 8 cm. Kahlbaum's crystallized sulphur contains volatile impurity. The reductions, for pressure, of the boiling points of sulphur and of water were made in accordance with the data of Holborn and Henning.[4] As the constants of the platinum thermometer are known to be changed by prolonged heating, the fixed points were redetermined whenever the thermometer had been kept long at high temperatures. The following figures will give an idea of the degree of constancy of the thermometer used, and relate to an epoch when the thermometer was being heated at temperatures of 300°–445° for many consecutive hours: 1909, October 8th, $R_0 = 50.1150$ ohms; Oct. 18th, $R_0 = 50.1161$; Oct. 22nd, $R_0 = 50.1170$. Here the total change amounts to 0.01°. The corresponding values of

[1] *Ann. Physik*, [3] **26**, 833 (1908).

[2] See Callendar and Moss, *Proc. Roy. Soc. A*, **83**, 106 (1910); Waidner and Burgess, *Bull. Bureau of Standards*, **6**, 149 (Nov., 1909).

[3] See Eumorfopoulos, *Proc. Roy. Soc. A*, **81**, 339 (1908); Waidner and Burgess, *Loc. cit.*

[4] *Loc. cit.*

[illegible]

mandril-drawn, seamless steel tube, 18 mm. in diameter and over 2 m. in length, which was fixed in a truly vertical position. This steel tube, along with the steel tape, gage, and mirror were attached to a long board, which was suspended by a rope and balanced by a counterweight. The whole gage could thus be moved vertically between guides, in such a way as to bring to the level of the eye the point at which the mercury stood. This kept the mercury accessible to convenient observation during the numerous manipulations connected with a reading. By the use of the cursor described above the somewhat tedious use of a cathetometer was avoided, with no sacrifice of accuracy.

The heated air arising from the bath passed directly into the flues of a draught cupboard, within which the bath stood, and did not reach the gage, which was outside the cupboard. Moreover, the gage was shielded from heat radiated by the bath.

Pure mercury from the laboratory supply was redistilled *in vacuo* before use in the gage, and was tested by the method of Hulett and Minchin.[1] A portion was redistilled twice in air to oxidize the more electropositive metals, if present. The potential difference between the two samples, when placed in *N* KCl solution saturated with calomel, was less than 0.000003 volt. The metal was, therefore, of a satisfactory degree of purity.

Since an open gage was used, the barometric height had to be read. The instrument was one made by Henry Green, of Brooklyn. The scale was already corrected for capillarity. The instrument was standardized by comparison with a barometer, in which the tube was exhausted by means of a mercury pump until the McLeod gage showed a residual pressure of less than 0.003 mm. The reading of the Green barometer was found to be correct.

The following corrections were applied to the pressures:

1. The pressures were reduced to mm. of mercury at 0°. For this purpose five carefully compared thermometers, graduated to tenths of a degree, were suspended at intervals along the gage. To eliminate differences in mass and lag between the thermometers and the mercury in the gage, the bulbs of the thermometers were immersed in mercury contained in tubes of the same diameter as the gage. The coefficient of linear expansion of mercury used was 0.0001818. The error in density of mercury due to its compressibility is negligible at the pressures employed.

2. The coefficient of linear expansion of steel used in calibrating the steel tape was 0.000011.

3. The mercury heights were reduced to the sea level at 45° N. L. The value of the gravity constant, *g*, determined in the Ryerson Physical

[1] *Physic. Rev.*, **21**, 388 (1905).

Laboratory of the University, namely 980.34, agrees precisely with that calculated from latitude and elevation. The value of $g$ taken as the standard[1] was 980.665 cm. sec.$^{-2}$, and the factor by which the observed heights were multiplied was therefore 0.99967. The amount of this correction is thus 0.25 mm. per 760 mm.

4. In measuring the vapor pressures of water, since the temperature error in that case was less than $\pm 0.01°$, suitable correction was made for the difference in level between the cistern of the barometer and the mercury in the open limb of the gage. A similar correction was made, when necessary, for the difference in level between the surface of the water in the bulb of the isoteniscope and the surface of the mercury in the closed limb of the gage. The amount of this correction is about 0.09 mm. per meter head of air.

**Other Parts of the Apparatus.**—The general arrangement of the apparatus is shown in Fig. 3, which is diagrammatic. The isoteniscope and the gage were connected with a large iron bottle. Another piece of tubing leading from the bottle gave connections, by means of T-tubes, with (1) the atmosphere, (2) a vacuum reservoir and water pump, (3) a pressure reservoir, and compression pump. A stopcock on the first, and screw clamps on each of the other two tubes permitted any one to be used at will. The rubber tubing leading to the atmosphere was so long that it hung out over the edge of the base of the draft cupboard.

The water pump, with its residual pressure of about 20 mm., according to the temperature of the water, served our purpose very well, as no measurements of vapor pressures below 80 mm. were to be made. With a mercury pump, much lower vapor pressures could be studied with the same arrangement of the rest of the apparatus.

The connections were made with thick-walled rubber tubing, wired at all junctions, and coated heavily with a suitable composition. No tendency to leakage was ever observed.

**The Manipulation.**—The following statements apply particularly to the determinations of the vapor pressures of water below one atmosphere. The modifications required when pressures over one atmosphere are measured, or when another liquid or a solid is used, will be understood without special description.

When the temperature has reached the desired point, and has become constant, the exit to the suction bottle and pump is opened and remains open until the pressure in the iron bottle has been reduced to such a point that the water in the bulb boils, and the vapor passes freely through the confining fluid (itself also water) in the U-tube. The confining fluid is driven into the remote side of the U-tube and the bulb above it. When

[1] Troisième conf. gén. des poids et mésures, 1901, 66, 68.

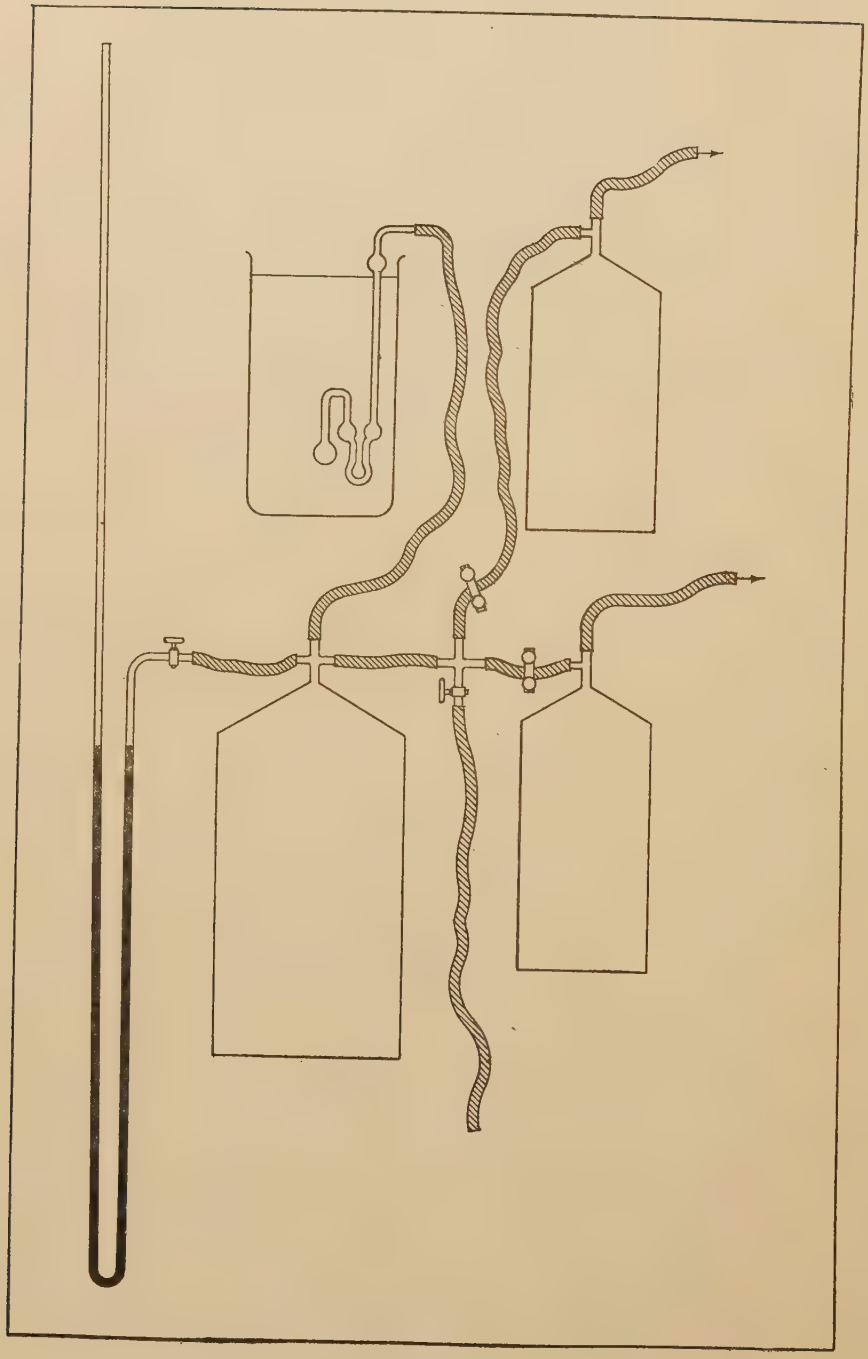

Fig. 3.

the air in the bulb, and the gases adhering to the bulb and dissolved in the water have been driven out, air is cautiously admitted to the iron bottle through the exit to the atmosphere until the levels of the water in both limbs of the U-tube are identical. On account of the cooling of the substance in the bulb by evaporation, equilibrium is not reached at once, so that the adjustment has to be repeated until the levels in the U-tube remain constant. The finer adjustment is not easy to manage by the use of the stopcock alone, and the long rubber tube opening to the air is employed. When, for example, a slight increase in pressure is required, the tube is grasped with the hands at two places and air is admitted to the bottle in small portions at a time until equilibrium is attained.

When the adjustment has been perfected, the stopcock on the gage is closed, the temperature reading is confirmed, and the gage and barometer are read. Within the time required for making the gage reading, no variation occurred in the level of the mercury due to a change in temperature in the air confined in the closed limb. To make sure that volatil foreign matter or gas has all been expelled, the whole process of boiling out, adjusting, and reading is repeated until constant values are obtained.

The temperature of the bath is then raised, and a new observation taken. Unless the substance is unstable, and decomposition products arise, repeated boilings at the second and higher temperatures produce no change in the values first obtained.

### Section 4. Criticism of the Method.

It will be seen that the isoteniscope is free from the sources of error which affect the older forms of apparatus for determining vapor pressures. For example:

1. The isoteniscope substitutes for mercury a confining fluid of low specific gravity and thus eliminates the error in leveling involved in some static methods.

2. The apparatus dethrones mercury from its position as sole confining fluid, and substitutes a wide choice of liquids. In consequence, all errors due to the volatility of a foreign confining fluid, and to solubility of the substance in, or interaction of, the substance with such a confining fluid disappear entirely.

3. By being adapted to use in a liquid bath (with violent stirring), the apparatus reduces to a minimum all errors due to unsteadiness of the temperature, and to inequality in the temperatures of the substance, its vapor, and the thermometer.

4. By providing a simple method for expelling air bubbles and adhering and dissolved gases, and for repeating the expulsion until the success of the operation is demonstrated, the isoteniscope removes a source of

error (and of total uncertainty as to the amount of that error) which destroys all confidence in the exactness of the results obtained by the older static methods.

5. By permitting the making of an extended series of observations without using more than half of the sample, the apparatus obviates an error due to concentration of involatil impurities in the residue which affects some dynamic methods.

6. By allowing the expulsion of accumulated gas immediately before a reading, the apparatus makes possible accurate measurements with many substances which decompose slowly to give a permanent gas. By the older static methods, accurate measurements in such cases was necessarily impossible.

Aside from this avoidance of certain sources of error, the apparatus possesses some noteworthy advantages:

1. A small amount of material suffices (usually less than 1 gram).

2. The filling of the apparatus, and the manipulations involved in a measurement, are incomparably simpler than any other static method.

3. The correction for dilatation of the bulb of the mercury thermomter (the so-called "pressure" coefficient), which some dynamic methods involve, is avoided.

4. Since, with liquids, no foreign substance (such as mercury) is present, the method permits measurements with all reasonably stable liquids, no matter how active, chemically, they may be.

5. The method is applicable to all solids, provided a non-interacting, non-solvent, non-volatil confining liquid can be found. When such a liquid cannot be found, a dynamic method to be described in a later paper ("Studies in Vapor Pressure, III") may be used.

### Section 5. The Vapor Pressures of Water.

On account of the facts about water, some of which were brought out in Section 1, namely the ease with which natural impurities are removed, the relatively slight solubilities of gases in water, the more normal behavior of water as shown in the work of Tammann and of Wüllner and Grotian, and the relatively slight inconsistencies in the existing determinations of its vapor pressures, water is a suitable substance for affording a test of the merits of the method. Moreover, no other substance combines all these qualities, and water is therefore at present the only suitable substance.

There is no reason why mercury should not equal, or even excel, water in freedom from impurities and in regularity of behavior. Only the inconsistencies in the measurements which thus far have been made, and especially the utter disagreement of those above the boiling point, render it unsuitable for comparing methods.

**Results.**—The isoteniscope was thoroughly steamed out, and distilled water, giving no appreciable residue on evaporation, was redistilled into it. The method itself provides for the expulsion of dissolved gases. The measurements were made with the apparatus described above, and the corrections before mentioned were applied.

The observations were made by design as close as possible to temperatures, the values of which should be represented by whole numbers. The differences for one-tenth of a degree at each temperature, taken from Eckholm's[1] tables, were then used in making the very small adjustments required to reduce each observation to the nearest whole number of degrees. The results of this operation are given in the following table (I) under S & M. The pressures in this column, therefore, are not smoothed results, such as may be obtained by graphical or other methods, but are essentially *actual observations*, subject to the irregularities which individual observations usually show. This enables them to afford the most rigorous test of the method, while the adjustment facilitates the comparison with the data of other observers, which are usually given for whole degrees. The twenty-seven observations give, after adjustment, values at eleven different temperatures.

TABLE I.

| | M. | | | Differences, H & H—M. | |
|---|---|---|---|---|---|
| *t.* | No. of obsns. | *p.* | H & H. | mm. | Degrees. |
| 50° | 3 | 92.27 | 92.30 | +0.03 | —0.006 |
| 51 | 4 | 97.03 | 96.99 | —0.04 | +0.009 |
| 55 | 1 | 117.87 | 117.85 | —0.02 | +0.004 |
| 60 | 2 | 149.13 | 149.19 | +0.06 | —0.010 |
| 65 | 3 | 187.19 | 187.36 | +0.17 | —0.019 |
| 70 | 3 | 233.44 | 233.53 | +0.09 | —0.009 |
| 75 | 1 | 288.78 | 289.0 | +0.22 | —0.018 |
| 80 | 1 | 354.90 | 355.1 | +0.20 | —0.014 |
| 85 | 3 | 433.54 | 433.5 | —0.04 | +0.002 |
| 89 | 5 | 505.87 | 506.1 | +0.23 | —0.011 |
| 90 | 1 | 525.94 | 525.8 | —0.14 | —0.007 |

For comparison, we give under H & H the corresponding values found by Holborn and Henning[2] in the *Reichsanstalt*. These are undoubtedly the most accurate in existence. Their temperature scale is the same as ours. Their results are smoothed values, derived from numerous observations. The greatest divergencies are 0.23 mm. and 0.019°. The algebraic sum of all the temperature differences, divided by the whole number of our observations (27), gives the mean divergence from H & H's curve of a curve drawn through our observations. This mean di-

[1] *Svensk. Vet. Akad., Arkiv. för Math., Astron., och Fysik*, Band 4, Häfte 2, No. 29 (1908).

[2] *Ann. Physik*, [4] 26, 833 (1908). The reason for accepting these values as the most accurate will be apparent to any one who considers the details of the method used

vergence is —0.0063°, which is well within the error which we assign to our measurement of absolute temperature (±0.01°). The corresponding mean pressure deviation is +0.08 mm. This agreement is of especial interest since our method is static, while theirs was dynamic.

**Comparison of Other Methods.**—We may now institute a comparison between the results obtained by our method and those obtained by others, using Holborn and Henning's values as the standard of comparison.

Taking first the static methods, with which ours may most justly be compared, there are only two sets which included the region 50°–90°, namely those of Magnus and of Batelli. In both cases mercury was the confining fluid, and the U-tube form of vaporizing vessel was used. Magnus[1] boiled the mercury "well" after its introduction. He also boiled the water for 1/2–3/4 hour, and then introduced it, while yet warm, through the open limb, by inclining the apparatus. Batelli[2] "caused the mercury to boil several times." The water was introduced in a small glass bottle, after elaborate purification and subsequent boiling for twenty-four hours. No precautions to remove gases adhering to the small bottles are mentioned.

In the first two columns of the following table (Table II), only the differences between the pressure values of Holborn and Henning and those of Magnus (M) and of Battelli (Ba), respectively, are given. These numbers are to be added to the published data, to give those of H & H. The other columns will be explained presently:

TABLE II.

(Differences from H & H.)

| | Static. | | Dynamic. | | Recalculations. | | |
|---|---|---|---|---|---|---|---|
| *t.* | M. | Ba. | Rg. | W. | Br. | T. | E. |
| 50° | +0.33 | +1.85 | +0.28 | ... | +0.32 | —0.22 | —0.34 |
| 60 | +0.61 | +2.3 | +0.36 | ... | +0.31 | —0.19 | —0.38 |
| 70 | +0.92 | +2.7 | +0.58 | ... | +0.22 | —0.14 | —0.40 |
| 80 | +1.2 | +2.7 | +0.5 | —0.3 | +0.2 | 0.0 | —0.34 |
| 90 | +1.0 | +2.1 | +0.3 | —0.2 | +0.3 | 0.0 | —0.2 |
| Av. | +0.81 | +2.3 | +0.4 | —0.25 | +0.27 | —0.11 | —0.33 |

The average divergencies from H & H are: Magnus +0.81 mm. (or —0.07°), Batelli +2.3 mm. These are respectively ten and thirty times as great as our average divergence. It must be noted that the data of these two observers are all smoothed values.

Schell and Heuse[3] have recently determined the value at 50° (92.54 mm.) by a static method. Our value (static) confirms that of H & H.

[1] *Pogg. Ann.*, **61**, 225 (1844).

[2] *Ann. chim. phys.*, [6] **26**, 410 (1892); [7] **3**, 408 (1894).

[3] *Ann. Physik*, [4] **31**, 715.

On account of the extensive use which has been made of Ramsay and Young's static methods, both by themselves and by others, a comparison would be very instructive. Their barometer tube method, available up to nearly 760 mm., with the special device for filling so as to exclude foreign gases, was not applied to water, which is the only suitable substance for making a rigid comparison. Their only determinations with water[1] begin at 120°, and are therefore not directly comparable with ours. The filling of the tube[2] involved boiling of the substance, but not of the mercury in the tube. The differences between their values and those of H & H at their lowest temperatures are as follows: 120°, +4.9; 130°, +6.6; 140°, +15.5; 150°, +0.7. The average divergence is +6.9 mm., or —0.1°, and is of the same order as that of Magnus. These, again, are smoothed values. This divergence is not due to the difference between the scales of temperature used by Ramsay and Young (const.-vol. air-therm.) and by H & H, for this would not exceed 0.014° (corresponding to 1.3 mm.) even at 150°, and besides, if taken into account, would increase the divergence.

If we turn now to results obtained by dynamic methods, there are only three sets which include the region under consideration, namely those of Regnault, Wiebe (82°–100°), and Holborn and Henning. Regnault's[3] dynamic observations extended from 43° to 230°. In the column headed Rg of the foregoing Table II, we give the differences between the data of H & H and of Regnault, using for the latter the data calculated by the "H" formula. This was the formula which Regnault found most generally satisfactory, and it appears to be especially so within the region in question. Wiebe[4] made measurements from 82° to 100° only. His results (Col. W), however, seem to be considered especially good by H & H, and they are weighted very heavily in Eckholm's recalculation of the data which he considered. The average divergences from the results of H & H are: Regnault, +0.4 mm. (or —0.04°), and Wiebe —0.25 mm.

On account of the very large number of measurements made by Ramsay and Young, and by other observers, with their dynamic method,[5] in which the thermometer bulb is surrounded by cotton saturated with the substance, a comparison of its performance with that of other methods is extremely desirable. Unfortunately, although they made a series of observations with water,[6] they give no results and content themselves with stating that the values were "identical with those of Regnault."

[1] *Phil. Trans.*, *A*, **183**, 107 (1892).
[2] *Ibid.*, *A*, **178**, 57 (1886); Young, *Stoichiometry*, 134 (1908).
[3] *Rel. des Experiences*, **1**, 465 (1847).
[4] *Z. Instrumentenkunde*, **13**, 329 (1893).
[5] See Section 2 of this paper.
[6] *Phil. Trans.*, **175**, 48 (1884).

It is a pity that they did not state more exactly the degree of approximation, and specify which of the appreciably divergent sets of data were used in the comparison—for example, the curve, the values calculated by "formula H" (those most commonly quoted, *e. g.*, in the *Chemiker Kalendar* and Van Nostrand's *Chemical Annual*), or Brock's recalculation (adopted by Ostwald in his *Handb.*). As we have seen, however, the method is open to serious criticism.

Finally, in the last three columns (Table II) we give the results of Regnault, as recalculated by Brock (Br), the data of all previous observers as combined and recalculated by Thiesen[1] (T), which were adopted without change up to 100° by Henning[2] in his most vigorous study of the same data, and the results of Eckholm's (E) recalculation of the same data. As before, only the differences, H & H—Br, etc., appear.

This comparison shows that, assuming Holborn and Henning's values to be correct, the results by our method lie much closer to the true value than do those by any other static method. They likewise diverge much less than do the results of the recalculations of previous determinations. They lie also much closer than do the values obtained by the dynamic methods, although all writers are agreed that the dynamic methods give more trustworthy results than do the static ones which have hitherto been employed.[3]

The degree of self-consistency of the observations may be seen by inspection of Table I. A more detailed study of the deviations from a smooth curve of the individual observations obtained by this method will be undertaken in the following paper on mercury.

To determin definitly the merits of the isoteniscope, *per se*, it would be necessary to eliminate from the older observations the effects of the errors in the measurements of temperature and of pressure, and to isolate the error due to the form of the vaporizing chamber and the method of handling the substance. It is unfortunately impossible to do this. It is to be noted, however, that the gage and thermometer errors are common to static and dynamic methods, and should be essentially alike in both. Now the average magnitude of the divergencies of the dynamic and static methods, respectively, from that of H & H are 0.33 mm. and

[1] *Ann. Physik*, [3] **67**, 692 (1899).

[2] *Ibid.*, [4] **22**, 609 (1907). This was before the redetermination by Holborn and Henning.

[3] The much closer approximation of our results to those of H & H is not due to the fact that the same scale of temperature was used by both, whereas the other observers used air thermometers (Regnault, a mercury thermometer). The difference between the scales at 50°–90°, except possibly in the case of Regnault's values, is so small that it would equal only a fraction of the divergence in each case, and besides, wherever the differences in pressure are positive in the preceding tables, an adjustment to the thermodynamic scale would only increase the divergencies.

1.55 mm. The excess of the static over the dynamic may perhaps be held roughly to represent the minimum value of the error of the older static methods *per se*. Now this difference is 1.22 mm., or about fifteen times the total divergence of our results due to all causes.

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## STUDIES IN VAPOR PRESSURE: II. A REDETERMINATION OF THE VAPOR PRESSURES OF MERCURY FROM 250° TO 435°.

Both for practical and theoretical purposes, an exact knowledge of the physical constants, and particularly of the vapor pressures of mercury, is of the greatest importance. Mercury is used in innumerable ways in research and in many instances the accuracy of the results depends on a knowledge of the vapor pressures of this substance. Since mercury shows no evidence of a tendency to association, and since its vapor is monatomic, presenting in the former respect a great contrast to water, and in the latter respect even to the liquids of more normal behavior, like benzene, an exact knowledge of its vapor pressures should be of the utmost value in the study of the laws pertaining to vaporization. The relations, for example, between temperature and pressure and between these two and heat of vaporization, on account of the absence of complicating factors, should be of special simplicity in the case of mercury. Moreover, it is more easily obtained in a state of extreme purity than almost any other substance. Yet, in spite of all this, as Laby says, "the greatest—and it should be added, unnecessary—disagreement is to be found in the current values of this vapor pressure." For these reasons, and because accurate data were required for a study of calomel vapor which will shortly be published, a redetermination of the vapor pressures from 250° to 435° was undertaken. The range chosen was limited to the region required for this special purpose, but we intend later, with a longer gage, to extend the series. The theoretical study of our results is postponed until the longer series shall be available.

**Previous Determinations.**—The work of previous observers has been subjected to a critical study and their data have been combined by Laby.[1] We are not concerned with the values at low temperatures, of which those of Pfaundler,[2] Morley,[3] and Hertz[4] (the latter's extend to 207°) are in excellent agreement, and are irreconcilable with the erratic values of

[1] *Phil. Mag.*, [6] **16**, 789 (1908).
[2] *Ann. Physik*, [3] **63**, 36 (1897).
[3] *Phil. Mag.*, [6] **7**, 662 (1904).
[4] *Ann. Physik*, [3] **17**, 193 (1882).

Van der Plaats,[1] Hagen,[2] and McLeod.[3] As regards Regnault's[4] three low-temperature series, including observations up to 205°, he himself states that they give data that are only approximate. The series of determinations discussed below are those which touch the region covered by our experiments. The data themselves will be found in a comparative table (Table VI) given towards the end of the paper.

Regnault's values at the highest temperatures are based, (1) on four old determinations of the boiling point of mercury (about 357°) made with an air thermometer, two of which differ by about 2° at the same pressure, and (2) a new series from 251° to 511.7°. In the latter, the mercury boiled under varying air pressures. The temperatures were determined with a constant-volume air thermometer. The boiling metal began to bump occasionally at 345° and violently at 428°. The values near the ordinary boiling point are obviously discordant, as the three following observations show: 354.60°, 758.20 mm.; 354.83°, 761.87 mm.; 356.69°, 754.43 mm. Later workers have made much of Regnault's statement that his results were inaccurate, but he makes no such admission in regard to these two sets of values, leaving them to speak for themselves. All he says is that the experiments were not done in the same way as those which he made with other substances, because, when the bulb of the thermometer was surrounded by vapor, constant temperatures could not be obtained, and in this case, therefore, the bulb was completely below the surface of the liquid. Owing to the great depth of the mass of mercury (50 kilos), the lowest layers must have been seriously superheated.

Ramsay and Young's[5] well-known series of vapor pressures of mercury was based upon four groups of observations. Young, in a paper which appeared five years after and seems to have escaped notice,[6] utilized later values for a part of the fundamental data, and gives a corrected and very considerably altered table (see Table VI). The four original groups of observations were:

1. Four static measurements with mercury in a U-tube[7] heated by the vapor of methyl salicylate boiling at a known pressure. The temperature of the vapor was ascertained indirectly from a previously determined p.-t. curve. This p.-t. curve not having given satisfactory

[1] *Rec. trav. chim.*, **5**, 149 (1886).

[2] *Ann. Physik*, [3] **16**, 610 (1882).

[3] *Brit. Assoc. Rep.*, **1883**, 443.

[4] *Mem. Acad. Sci.*, **21**, 30, 502 (1847); **26**, 506 (1862).

[5] *J. Chem. Soc.*, **49**, 37 (1886).

[6] *J. Chem. Soc.*, **59**, 629 (1891). Not referred to in Landolt and Börnstein, [3] (1905), nor in Abegg's *Handb.*, II, ii (1905), which give the old set of values.

[7] For proof of the difficulty in excluding foreign gases from such a tube see preceding paper, Sec. 2.

results in other cases, Young, in the second paper, discards these observations and substitutes for them two new readings with aniline vapor as the heating agent at 183.7° and one with quinoline vapor at 236.9°. These temperatures (const.-vol., air-therm. scale) are therefore ascertained indirectly as before.

2. Two static measurements with mercury in a U-tube heated by the vapor of bromonaphthalene boiling at known pressures. It is a little difficult to make out the exact status of this part of the data. These were old observations, originally made as part of a study of the vapor pressures of bromonaphthalene.[1] On that occasion, the temperature corresponding to the observed bromonaphthalene pressure was ascertained by taking from Regnault's formula the temperature at which mercury exercised the vapor pressure observed in the U-tube. These, along with three other series of measurements made in a different way, were employed in making the bromonaphthalene p.-t. curve. They entered directly into the making of the curve, and were used also for ascertaining the correction of an English thermometer employed in one of the other (the fourth) series.

On the present occasion they play the reversed roles of measurements of the vapor pressure of mercury. One of these agrees with the final p.-t. curve of bromonaphthalene and the other is adjusted by altering the temperature 0.4° to bring it onto this curve. As these results are retained and used by Young in the second paper, it is necessary to consider their probable accuracy.

The values, as adjusted, were considered to be correct for two reasons. One was because they gave normal results when used in the study of certain vapor pressure relations of water and bromonaphthalene, expressed by the formula $R' = R + c\ (t'—t)$.[2] But water is an abnormal substance and is admitted to be unsuitable for the study of this relation,[3] so that the agreement of the results with the theory in this instance affords no guarantee of the accuracy of the data. The vapor pressures of mercury adopted on the basis of this observation, when compared with those of water in the light of the same relation, again showed good, but, for the same reason as before, unavailing agreement with the theory. The value of the results must be judged, therefore, solely by the other reason for considering them correct, namely, the accuracy of the p.-t. curve of bromonaphthalene on which they are based.

This curve[4] is founded on several series of observations. Two series were made by Ramsay and Young's dynamic method,[5] in which the

[1] *J. Chem. Soc.*, **47**, 65 (1885).
[2] *Phil. Mag.* [5], **20**, 515 (1885); **21**, 33 (1886).
[3] Young, *Stoichiometry* (1908), 144.
[4] *J. Chem. Soc.*, **47**, 646 (1885).
[5] For detailed criticism see preceding paper, Sec. 2.

thermometer bulb is surrounded by cotton and immersed in the vapor. No correction for dilatation of the bulb[1] is mentioned, but its absence would not affect the results at 280°, with which we are concerned, as the pressure is there atmospheric. The objections on account of the introduction of dissolved gases along with the liquid, and of the gradual concentration of impurities, however, still remain. The results of the second series are below those of the first by 0.8° at 278°. In the fourth series, the bromonaphthalene boiled in a tube under known pressures and its temperature was ascertained by means of a thermometer immersed in the vapor. This was the thermometer standardized by assuming Regnault's vapor pressure curve of mercury to be correct. The results are above those of the second series at 280° by 1.9°. The temperatures in these series were all reduced to the constant-volume, air-thermometer scale. The third series consisted of the pair of observations first referred to.

It appears, therefore, that these two observations are not independent of the p.-t. curve of bromonaphthalene, and that the latter is made from data diverging as much as 1.9° at 280°.

In a later paper, Young[2] refers to certain discrepancies in results obtained by the use of the p.-t. curve of bromonaphthalene vapor, which he believes to be due to a slight underestimation of the temperatures at 280°. Table IV, however, will show that these two sets of observations from 183.7 to 280° are probably much more accurate than those of Hertz in the same region.

3. The third group of data pertaining to the vapor pressures of mercury used by Ramsay and Young consisted of the four boiling points of mercury originally employed by Regnault, two of which differed by 2° at the same pressure. Young, in the later paper, rejects these and substitutes Callendar and Griffiths'[3] determination of the boiling point of mercury at 760 mm., reduced to the sea level at latitude 45°, the value of which is generally quoted as 356.76° (const.-press. air-therm. scale). In this work, the details of which cannot be discussed here, the authors used values obtained with four improved platinum resistance thermometers, each compared in the vapor of boiling sulphur and at 0° and 100° with a constant-pressure air-thermometer. The mean result, reduced to the basis of the S b. p. = 444.53°, which the same observers had determined, was 356.76°. The mean of the results with five earlier, trial platinum thermometers, similarly reduced, was 356.74°. A final set of three "very careful" observations with a new platinum thermometer gave the mean value 356.73°. The final mean value with the five best ther-

[1] *J. Am. Chem. Soc.*, **32**, 905.
[2] *J. Chem. Soc.*, **77**, 1147 (1900).
[3] *Phil. Trans.*, *A*, **182**, 150–2 (1891).

mometers is 356.74°, in exact agreement with that of the five earlier instruments.

4. The fourth, and last, of the groups of observations used by Ramsay and Young consisted in two static measurements of the vapor pressure of mercury when heated by boiling sulphur. For the temperature, Regnault's boiling point of sulphur, 448.34°, the only one then available, was used. Young retains the pressure data and substitutes Callendar and Griffiths'[1] value for this boiling point (444.53°). According to Ramsay and Young's table, a difference of 4°, such as this, corresponds to a change in pressure at 445° of 139 mm. Hence this substitution greatly altered the value at 445°, as well as all the values between 760 and 2850 mm., which, in the absence of intermediate determinations, were all obtained by interpolation.

The vapor pressures were determind by heating the mercury in an apparatus shaped like a round-bulbed thermometer, with the stem bent into a horizontal position. The mercury, when cold, filled the bulb and a part of the stem, and was driven along the latter, compressing the air in the end, when mercury vapor was formed in the bulb. The bulb and a portion of the non-horizontal part of the stem of this thermometer-shaped apparatus were surrounded by the vapor of sulphur boiling in a vessel which in one experiment was a flask and in the other a wide test tube. Dr. Young, whom we desire to thank for most courteously giving us additional information on a number of points, states that the air column, before compression, was approximately 400 mm. in length. At four atmospheres pressure its length was thus reduced to 100 mm. Since the reading was probably accurate to ±0.1 mm., the pressure error should be only ±1 in 1000, or about 3 mm. The accuracy of the pressure reading was therefore satisfactory.

It is unquestionable, however, that in assuming that the bulb was really heated to 444.53° by the arrangement used, a serious error is introduced. The flask and test tube containing the boiling sulphur were not covered or protected in any way. Now, Callendar and Griffiths devote much space in their paper to a detailed description of their observations on this point. They used a Victor Meyer vapor density tube 4 cm. in diameter. Even when such a tube was padded externally with asbestos to retain the heat, the temperature reached by the thermometer was only 442.38°. They showed that the temperature of their thermometer (corresponding in Ramsay and Young's experiment to the bulb) was reduced by the trickling down of condensed, cooled sulphur and by radiation to the layer of condensed sulphur on the walls. By introducing a little hood to divert the sulphur running from the stem, and two cylindrical screens (one of metal and one of glass) to stop radia-

[1] *Phil. Trans.*, *A*, **182**, 119 (1891). See also preceding paper, Sec. 3.

tion, they finally brought the observed temperature up to 444.53°. In Ramsay and Young's experiment, therefore, the temperature actually reached was probably not far from 442.38°, or about 2° short of the value assigned to it by Young.

Gebhardt[1] boiled mercury in a glass globe. The temperatures of the vapor were taken with "a thermometer," presumably a mercury thermometer. No attempts to standardize the instrument, or to correct the readings for exposed thread or dilatation are described. Corrections of the gage are likewise lacking. But the pressures are given to tenths of a millimeter (see Table II).

Cailletet, Colardeau, and Rivière[2] determined, by a static method, the vapor pressures in atmospheres from 400° to 880°. The results are of interest as showing the order of the pressures at very high temperatures. The authors state that their results are sensibly the same as Regnault's, so far as the latter extend. Laby used these results although he rejected Regnault's, and this accounts for the fact (see Table VI) that above 360° his figures are higher than those of Young. No information as to the values assumed for the fundamental points, or as to the scale of temperature employed, is given.

Summarizing the history of this subject, we find that our knowledge of the higher vapor pressures of mercury rests on no very secure foundation. The boiling point at 760 mm. is the only point ascertained with precision. Not one observer makes any statement in regard to the purity of his mercury. Aside from Callendar and Griffiths, Regnault is the only investigator who states what he did in every experiment with perfect lucidity and completeness. Unfortunately, his results at closely adjacent points are inconsistent, his temperatures are those of the liquid and not of the vapor, and his air thermometer was inexact in its readings.

**The Vapor Pressures of Mercury.**—The apparatus used was identical with that described in the preceding paper.[3] The U-tube of the static isoteniscope contained mercury. The mixture of potassium and sodium nitrates was used as the bath liquid. The vibration communicated from the stirrer prevented bumping, which otherwise might have occurred when the metal in the bulb was allowed to boil.

The mercury, already distilled *in vacuo*, was redistilled in the same way at the rate of 30 cc. per hour. It was then washed ten times with dilute nitric acid in a tube 1.3 meters long, by the method recommended by Hildebrand.[4] This method is like Ostwald's excepting that the metal

[1] *Ber. physik. Ges.*, **7**, 184 (1905).
[2] *Compt. rend.*, **130**, 1585 (1900).
[3] *J. Am. Chem. Soc.*, **32**, 1419.
[4] *Ibid.*, **31**, 933 (1909).

is strained through muslin, which divides it into extremely small streams, instead of being allowed to enter the acid in a single stream. It was then dried and tested by the method of Hulett and Minchin,[1] which is incomparably the most sensitive. A portion of the metal was distilled twice in air, which oxidizes the more active metals, if present. Samples of each lot were then placed in a cell containing *N* KCl solution saturated with calomel. The potential difference of the two samples was less than 0.000002 volt, the limit of sensitiveness of the galvanometer employed. The method is capable of detecting one part of zinc in $10^{10}$ parts of mercury, and corresponding amounts of other active metals. The mercury in the gage was also tested and found to be of a like degree of purity.

The corrections and the precautions, such as frequent redeterminations of the fixed points, were identical with those used in the observations with water which are recorded in the preceding paper.

Two series of readings, hereafter named the first and second series, were completed. In the first attempt to make the second series, the isoteniscope broke after the fourth reading. Since the next, and successful second series overlapped the first series for a considerable distance, rendering the four observations in the same region unnecessary, and since the instrument may have been defective before the breakage occurred, the four readings of the abortive series were not used. Aside from those four, every observation that was completed is recorded in Table I. The results, 43 in all, are given in the order of ascending temperatures, in which they were obtained. The members of the second series are distinguished by an asterisk.

It may be noted that an alteration in the zero of the thermometer, requiring a change of about 0.1°, occurred between the first and second series. On account of the overlapping, however, the individual observations are affected only to the extent of 0.05°. The aim was to secure observations with a temperature error of less than ±0.1°. The temperatures are worked to hundredths of a degree as, although not accurate to one unit in this place, the second decimal has nevertheless some significance.

The temperatures are on the thermodynamic scale, and assume the boiling point of sulphur to be 445° on that scale. If, later, a slightly different value for this point should be finally accepted, the preceding paper supplies the data required for any recalculation. If the S b. p. is taken 0.1° lower (*i. e.*, 444.9°), which is the present most probable value, then at 357°, for example, a correction of —0.06° is required.

The error of the individual gage readings, considered by themselves, is less than ±0.2 mm. The pressures are given to hundredths, although the second place has very little significance.

[1] *Physic. Rev.* **21**, 388 (1905).

**Critical Study of the Results.**—The observations were first plotted on a large scale, equivalent to a piece of cross-section paper 118 x 220 cm., and a smooth curve was drawn through them. This made easy the selection of three points, from which a Kirchoff-Rankine-Dupré formula was calculated. From this formula the pressures at every 2° in the region studied were reckoned. By linear interpolation, which is sufficiently accurate for intervals of 2°, the calculated temperatures corresponding to the observed pressures were then obtained. A study of the divergencies of the calculated and observed temperatures now showed that an alteration in two of the fundamental points would cause the formula better to fit the observations as a whole. With the very slightly altered points the whole process was repeated, and a further slight change in all three points was made. Thus, after two approximations, a final set of three points and a corresponding formula of a very satisfactory nature were secured. The fundamental points on which the final formula is based are:

264.16°, 106.52 mm.; 356.95°, 760 mm.; 433.96°, 2598.67 mm. The formula is $\log p = A + B/\theta + C \log \theta$, or, with the constants inserted:

$$\log p = 9.9073436 - 3276.628/\theta - 0.6519904 \log \theta, \qquad (R)$$

where $\log B = 3.5154272$; $\log C = \bar{1}.8142412$.

The following table contains: the reference numbers of the experiments (Col. 1), arranged in the order of ascending temperatures, with those of the second series distinguished by an asterisk; the observed pressures (Col. 2); the observed temperatures (Col. 3); the temperatures calculated with the use of the formula by the process indicated above (Col. 4); and the differences ($\Delta$) between the observed and the calculated temperatures.

If the formula fitted the observations exactly, the algebraic sum of the divergencies should be zero. It is actually +0.07°. A change of 0.003° in the middle point might improve the correspondence, but it did not seem desirable at present to attempt any such refinement.

Since the calculated temperatures lie on a smooth curve, the divergencies from them of the observed temperatures represent essentially the irregularities in the individual observations. A study of column 5 will, therefore, show the degree of consistency of the results. Of the forty-three observations, thirty show very small deviations, ranging from 0.00° to 0.05°. In eight cases the divergence is from 0.06° to 0.10°, in only five cases does it exceed 0.10°. Observation No. 37 is undoubtedly defective, on account of a misreading of the resistance or of the gage. The mean deviation from the smooth curve of a single observation (including No. 37) is 0.050°. This is well within the limit proposed for the accuracy of the absolute temperature measurements.

TABLE I.—THE OBSERVATIONS.

| No. | Press. obsd. | Temp. obsd. | Temp. calc. | Δ. | No. | Press. obsd. | Temp. obsd. | Temp. calc. | Δ. |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 82.08 | 253.97 | 253.91 | —0.06 | 23 | 747.81 | 355.98 | 356.05 | +0.07 |
| 2 | 96.84 | 260.35 | 260.36 | +0.01 | 24 | 765.44 | 357.32 | 357.34 | +0.02 |
| 3 | 106.52 | 264.16 | 264.16 | 0.00 | 25* | 769.26 | 357.72 | 357.62 | —0.10 |
| 4 | 117.04 | 267.99 | 267.96 | —0.03 | 26 | 817.00 | 361.04 | 360.99 | —0.05 |
| 5 | 128.57 | 271.82 | 271.81 | —0.01 | 27* | 836.43 | 362.43 | 362.32 | —0.11 |
| 6 | 141.05 | 275.68 | 275.66 | —0.02 | 28* | 885.76 | 365.62 | 365.58 | —0.04 |
| 7 | 169.82 | 283.61 | 283.55 | —0.06 | 29* | 932.66 | 368.54 | 368.55 | +0.01 |
| 8 | 210.79 | 293.07 | 293.04 | —0.03 | 30* | 1002.55 | 372.74 | 372.74 | 0.00 |
| 9 | 236.96 | 298.34 | 298.31 | —0.03 | 31* | 1008.68 | 378.66 | 378.69 | +0.03 |
| 10 | 273.24 | 304.75 | 304.86 | +0.11 | 32* | 1210.58 | 383.95 | 383.99 | +0.04 |
| 11 | 309.73 | 310.75 | 310.77 | +0.02 | 33* | 1265.60 | 386.66 | 386.69 | +0.03 |
| 12 | 334.92 | 314.33 | 314.51 | +0.18 | 34* | 1326.12 | 389.56 | 389.56 | 0.00 |
| 13 | 428.93 | 326.65 | 326.69 | +0.04 | 35* | 1425.97 | 394.04 | 394.07 | +0.03 |
| 14 | 457.10 | 329.87 | 329.91 | +0.04 | 36* | 1675.34 | 404.28 | 404.32 | +0.04 |
| 15 | 498.01 | 334.16 | 334.30 | +0.14 | 37* | 1744.34 | 407.17 | 406.94 | —0.23 |
| 16 | 537.55 | 338.21 | 338.27 | +0.06 | 38* | 1847.35 | 410.66 | 410.69 | +0.03 |
| 17 | 586.76 | 342.82 | 342.88 | +0.06 | 39* | 2037.15 | 417.17 | 417.19 | +0.02 |
| 18* | 635.00 | 347.13 | 347.11 | —0.02 | 40* | 2125.78 | 420.10 | 420.07 | —0.03 |
| 19 | 642.22 | 347.74 | 347.72 | —0.02 | 41* | 2334.34 | 426.52 | 426.47 | —0.05 |
| 20 | 697.73 | 352.13 | 352.23 | +0.10 | 42* | 2599.17 | 434.02 | 433.95 | —0.07 |
| 21* | 697.72 | 352.24 | 352.23 | —0.01 | 43* | 2624.35 | 434.71 | 434.65 | —0.06 |
| 22 | 732.13 | 354.85 | 354.87 | +0.02 | | | | | |

**Comparison with Other Methods.**—The qualities of the method used are best seen by applying the same mode of study to the observations of other observers. Cailletet, Colardeau, and Rivière do not publish their observations, but only the rounded results. Ramsay and Young's observations are not numerous enough for the purpose. Only in the cases of Regnault and Gebhardt[1] can the data be investigated as regards their consistency. In the following table (Table II) the observations of Gebhardt (taken from Laby's paper, as the dissertation is not accessible) are given. It contains the observed pressures (Col. 1), the observed temperatures (Col. 2), the temperatures calculated by the use of formula R (Col. 3), and the differences ($\Delta_1$) between the temperatures as observed and as thus calculated (Col. 4). The algebraic sum of these deviations divided by the number of observations is +0.81°, showing that the observed temperatures are on the whole 0.81° below those calculated.

A curve was drawn fairly to represent his results, and the divergencies of the individual observations from this curve are given under $\Delta_2$ (Col. 5). The sum of these divergencies is +0.2°, that is, approximately zero, as it should be. It will be noted that the individual temperatures, besides being, as we have seen, on the whole 0.81° too low, are exceedingly irregular. The mean deviation of a single observation from the smooth curve is 1.2°, or about twenty-four times as great as in the case of the present observations. The method is, in part, responsible for this.

[1] *Loc. cit.*

TABLE II.—GEBHARDT'S OBSERVATIONS.

| Press. obsd. | Temp. obsd. | Temp. calc. | $\Delta_1$. | $\Delta_2$. | Press. obsd. | Temp. obsd | Temp. calc. | $\Delta_1$. | $\Delta_2$. |
|---|---|---|---|---|---|---|---|---|---|
| 1.00 | 129.0 | 126.0 | —3.0 | —3.8 | 94.40 | 256.0 | 259.3 | +3.3 | +2.5 |
| 3.93 | 157.5 | 158.4 | +0.9 | +0.1 | 105.69 | 264.0 | 263.8 | —0.2 | —1.0 |
| 8.22 | 176.5 | 178.2 | +1.7 | +0.9 | 122.90 | 268.0 | 270.0 | +2.0 | +1.2 |
| 12.51 | 188.0 | 190.3 | +2.3 | +1.5 | 126.11 | 271.5 | 271.0 | —0.5 | —1.3 |
| 21.07 | 207.0 | 206.3 | —0.7 | —1.4 | 150.80 | 277.5 | 278.4 | +0.9 | +0.1 |
| 38.82 | 224.5 | 226.6 | +2.1 | +1.3 | 147.50 | 278.5 | 277.5 | —1.0 | —1.8 |
| 46.49 | 230.5 | 232.9 | +2.4 | +1.6 | 185.00 | 286.5 | 287.3 | +0.8 | 0.0 |
| 51.58 | 236.0 | 236.6 | +0.6 | —0.2 | 224.90 | 295.5 | 295.9 | +0.4 | —0.4 |
| 68.42 | 245.0 | 247.0 | +2.0 | +1.2 | 263.90 | 302.5 | 303.3 | —0.8 | —1.6 |
| 71.39 | 248.0 | 248.6 | +0.6 | —0.2 | 308.10 | 309.5 | 310.2 | —0.7 | —1.5 |
| 87.87 | 255.0 | 256.5 | +1.5 | +0.7 | 360.20 | 315.0 | 318.1 | +3.1 | +2.3 |

Regnault's main series (251° to 512°) is exhibited in Table III. Col. 3 contains the temperatures calculated by our formula, and Col. 4 the differences between the temperatures as observed and as thus calculated. The mean deviation of a single observation is 2.84°. Col. 5 shows the temperatures as calculated by Regnault's own formula (shorter form) and Col. 6 the differences between the temperatures as observed and as thus calculated. The mean deviation of a single observation from the smooth curve represented by Regnault's formula is 3.29°. Our formula thus fits his results better than does his own. The character of his work on this subject hardly justifies the extent to which his results have been quoted and used. It must be remembered, however, that he does not discuss their exactness, much less claim for them any special accuracy.

TABLE III.—REGNAULT'S OBSERVATIONS.

| Press. obsd. | Temp. obsd. | Temp. calc. (S & M). | $\Delta_1$. | Temp. calc. (Reg.). | $\Delta_2$. |
|---|---|---|---|---|---|
| 74.10 | 251.08 | 250.00 | — 1.08 | 249.15 | — 1.93 |
| 78.10 | 252.60 | 252.00 | — 0.60 | 251.26 | — 1.34 |
| 85.10 | 255.45 | 255.30 | — 0.15 | 254.71 | — 0.74 |
| 238.38 | 297.21 | 298.14 | + 0.93 | 299.28 | + 2.07 |
| 345.80 | 314.06 | 316.02 | + 1.96 | 316.88 | + 2.82 |
| 486.31 | 331.60 | 333.07 | + 1.47 | 333.83 | + 2.23 |
| 624.90 | 344.89 | 346.25 | + 1.36 | 346.84 | + 1.95 |
| 761.87 | 354.83 | 357.09 | + 2.26 | 357.48 | + 2.65 |
| 758.20 | 354.60 | 356.82 | + 2.22 | 357.22 | + 2.62 |
| 1529.60 | 412.96 | 398.50 | —14.46 | 397.70 | —15.26 |
| 2686.2 | 428.35 | 436.31 | + 7.96 | 433.96 | + 5.61 |
| 3180.6 | 444.06 | 448.51 | + 4.45 | 445.62 | + 1.56 |
| 4613.8 | 475.73 | 476.01 | + 0.28 | 472.74 | — 2.99 |
| 7316.7 | 511.67 | 515.75 | + 4.08 | 509.58 | — 2.09 |
| 6990.1 | 508.53 | 511.72 | + 3.19 | 505 75 | — 2 78 |
| 5966.2 | 499.88 | 498.13 | — 1.75 | 492.79 | — 7.09 |
| 754.43 | 356.69 | 356.54 | — 0.15 | 356.95 | + 0.26 |

**Comparison of all Observations.**—Since it thus appears that the present observations are probably of a relatively high order of accuracy, it is

instructive to compare the results of other observers. In the following tables are given all the published observations, omitting those of Regnault and most of Gebhardt's. The initials are those of the observers: Young (Y), Ramsay and Young (R Y), Hertz (H), Callendar and Griffiths (C G), Cailletet, Colardeau, and Rivière (C C R), Pfaundler (P), Morley (M).

In the first table (Table IV) appear the observations above 200°, with two others, and also the rounded values of C C R (no observed data having been published by them). Since in this region the chief experimental error lies in the measurement of temperature, rather than of pressure, the comparison is made in the same way as before.

TABLE IV.—OTHER OBSERVATIONS, CHIEFLY ABOVE 200°.

| Obsr. | Press. obsd. | Temp. obsd. | Temp. calc. | Δ. |
|---|---|---|---|---|
| Y..... | 9.94 | 183.8 | 183.62 | —0.18 |
| Y..... | 9.85 | 183 7 | 183.35 | —0.35 |
| H ..... | 20.35 | 203.0 | 205.29 | +2.29 |
| H..... | 22.58 | 206 9 | 208.56 | +1.66 |
| Y..... | 51.85 | 236.9 | 236.78 | —0.12 |
| RY..... | 124.35 | 270.35 | 270.43 | +0.08 |
| R Y..... | 157.15 | 280.2 | 283.23 | +0.03 |
| C G..... | 760 | 357.08 | 356.95 | —0.12 |
| C C R..... | 1596 | 400 | 401.00 | +1.00 |
| R Y–Y ..... | 2896.90 | 443.15 | 441.71 | —1.44 |
| R Y–Y ..... | 2904.50 | 444.15 | 441.92 | —2.23 |
| C C R..... | 3230 | 450 | 449.65 | —0.35 |
| C C R..... | 6080 | 500 | 499.7 | —0.3 |
| C C R..... | 10488 | 550 | 549.0 | —1.0 |
| C C R..... | 16948 | 600 | 599.4 | —0.6 |
| C C R..... | 25840 | 650 | 647.1 | —2.9 |
| C C R..... | 38000 | 700 | 696.3 | —3.7 |
| C C R..... | 77520 | 800 | 804.6 | +4.6 |
| C C R..... | 123120 | 880 | 889.6 | +9.6 |

Callendar and Griffiths' value is the mean of all their boiling-point observations reduced to thermodynamic temperature (S b. p. = 445°). None of the other temperatures have been reduced. At the high temperatures (C C R), where the reduction would make the most difference, no data are furnished by the authors. The values of the temperatures near 443–444° (Young) are about 2° too high, for the reason already given.

Table V contains all the observations below 200°. Since in this region the pressures are very low, the chief errors affect the pressures rather than the temperatures. In this table, therefore, the observed pressures (Col. 3) are compared with those calculated by formula R (Col. 4). The differences are given in column 5, and in column 6 is stated the percentage of the calculated value which was observed (*i. e.*, calculated value = 100).

TABLE V.—OBSERVATIONS BELOW 200°.

| Obsr. | Temp. obsd. | Press. obsd. | Press. calc. | Δ. | Percentage. |
|---|---|---|---|---|---|
| P..... | 15 | 0.00081 | 0.000844 | +0.000034 | 96.0 |
| M..... | 16 | 0.0010 | 0.000922 | —0.000078 | 108.5 |
| M..... | 30 | 0.0027 | 0.00298 | +0.00028 | 90.3 |
| M..... | 40 | 0.0052 | 0.00648 | +0.00128 | 80.2 |
| M..... | 50 | 0.0113 | 0.01339 | +0.00209 | 84.4 |
| P..... | 56.3 | 0.01807 | 0.02068 | +0.00267 | 87.1 |
| M..... | 60 | 0.0214 | 0.02648 | +0.0050 | 80.8 |
| M..... | 70 | 0.0404 | 0.0529 | +0.0125 | 76.4 |
| H..... | 89.4 | 0.16 | 0.1575 | —0.0025 | 101.6 |
| P..... | 98.8 | 0.26305 | 0.26220 | —0.0008 | 100.3 |
| H..... | 117 | 0.71 | 0.6552 | —0.0548 | 108.4 |
| G..... | 129 | 1.000 | 1.144 | +0.144 | 87.4 |
| H..... | 154.2 | 3.49 | 3.3280 | —0.162 | 104.9 |
| G..... | 157.5 | 3.93 | 3.718 | —0.212 | 105.7 |
| H..... | 165.8 | 5.52 | 5.216 | —0.304 | 104.3 |
| G..... | 176.5 | 8.22 | 7.732 | —0.488 | 106.4 |
| H..... | 177.4 | 8.20 | 7.985 | —0.215 | 102.7 |
| R Y..... | 183.4 | 9.87 | 9.8670 | —0.003 | 100.0 |
| H..... | 184.7 | 11.04 | 10.322 | —0.718 | 107.0 |
| G..... | 188 | 12.51 | 11.560 | —0.95 | 108.2 |
| H..... | 190.4 | 12.89 | 12.540 | —0.35 | 103.0 |

Morley's results were obtained by saturating carbon dioxide with mercury vapor. The calculated values seem to represent the results as a whole fairly well.

TABLE VI.—COMPARATIVE TABLE OF ROUNDED RESULTS.

| Temp. | Reg. | R & Y. | Y. | G | Laby. | M. |
|---|---|---|---|---|---|---|
| 255° | 85.9 | 85.0 | .... | ..... | 86 2 | 84.45 |
| 260 | 96.7 | 96.7 | 96.5 | 100.0 | 97.8 | 95.94 |
| 270 | 123.0 | 123.9 | 124.0 | 120.0 | 124.8 | 123.02 |
| 280 | 155.2 | 157.4 | 157.8 | 158.8 | 158.4 | 156.29 |
| 290 | 194.5 | 198.0 | 198.9 | 199.5 | 199.3 | 196.81 |
| 300 | 242.2 | 246.8 | 248.6 | 249.0 | 248.6 | 245.85 |
| 310 | 299.7 | 304.9 | 308.0 | 309.0 | 307.7 | 304.69 |
| 320 | 368.7 | 373.7 | 378.5 | ..... | 378.1 | 374.82 |
| 330 | 450.9 | 454.4 | 461.7 | ..... | 461.3 | 457.85 |
| 340 | 548.4 | 548.6 | 559.1 | ..... | 559.1 | 555.54 |
| 350 | 663.2 | 658.0 | 672.5 | ..... | 673.3 | 669.77 |
| 360 | 797.7 | 784.3 | 803.7 | ..... | 805.9 | 802.62 |
| 370 | 954.7 | 930.3 | 954.7 | ..... | 959.2 | 956.25 |
| 380 | 1140 | 1096 | 1228 | C C R | 1135 | 1133.0 |
| 390 | 1347 | 1284 | 1325 | ..... | 1337 | 1335.4 |
| 400 | 1588 | 1496 | 1549 | 1596 | 1566 | 1566.1 |
| 410 | 1864 | 1734 | 1801 | .... | 1826 | 1827.6 |
| 420 | 2178 | 2000 | 2085 | .... | 2119 | 2123.4 |
| 430 | 2533 | 2299 | 2403 | .... | 2446 | 2456.0 |
| 435 | 2728 | 2459 | 2572 | .... | 2628 | 2637.5 |
| 440 | 2934 | 2629 | 2757 | .... | 2817 | *2828.8* |
| 445 | 3153 | 2808 | 2939 | .... | 3018 | *3031.5* |
| 450 | 3384 | 2996 | 3150 | 3230 | 3229 | *3245.0* |

The preceding comparative table (Table VI) gives the smoothed results of various observers, for the most part for every ten degrees. It comprises only the region of the present experiments, with an extension of 450°, to include the boiling point of sulphur and two values by C C R. The values under M are calculated from formula R, and those which are extrapolated are in italics. Laby's recalculation took into account all the preceding data, excepting those of Regnault. But it will be seen that, above 340° at least, the errors in the latter are not as great as was at first suspected.

**The Boiling Point of Mercury.**—As considerable interest attaches to the knowledge of the exact boiling point of mercury at 760 mm., the values found for that point by different observers may be compared.

Regnault made seven measurements close to this point. The mean, when the results are reduced to 760 mm. and to thermodynamic temperature[1] (S b. p. = 445°), and when all are given equal weight, is 357.7°. The average deviation of a single observation from this mean is 1.34°.

Callendar and Griffiths' result with the five best thermometers, giving equal weight to each determination, is 356.74°. The correction to the thermodynamic scale (S b. p. = 445°) is about +0.34°, making the value 357.08°, with an average deviation of the individual observations from this mean of 0.02°. They believe that their absolute temperature measurement is correct ±0.1°. In judging of the probable accuracy of this value it is to be noted that they heated their mercury at th bottom with a small flame. The layer from which the vapor proceeded was therefore under a head of mercury indicated by the scale of their drawing to have been about 53 mm. The vapor was therefore probably superheated, and no mention is made of experiments to ascertain whether lowering or raising the thermometer altered the value of the observed temperature. We should expect, therefore, that their temperature would be, if anything, too high.

The present value, from the formula, is 356.95°, with the absolute temperature measurement believed to be accurate to ±0.1°. The possibility of superheating is here eliminated.

**Table of Smoothed Results.**—Finally, a table (VII) of the vapor pressures of mercury for every two degrees from 0° to 458°, calculated by formula R, is given. The extrapolated values, below 255° and above 435°, are in italics. The values below 255° probably represent, as we have seen, the somewhat divergent observations as well as would smoothed values made from these observations themselves. Intermediate values may be obtained by linear interpolation:

[1] As reduced by Dr. Edgar Buckingham, whom we have to thank for a private communication on the subject. His value, 357.1°, was on the scale S b. p. = 444.9°, and we have adjusted it to our scale.

TABLE VII.—VAPOR PRESSURES OF MERCURY FOR EVERY TWO DEGREES.

Temp. thermodynamic, press. mm. Hg at 0° and normal g. Extrapolated values in italics.

| Temp. | 0°. | 2°. | 4°. | 6°. | 8°. |
|---|---|---|---|---|---|
| 0° | *0.000207* | *0.000252* | *0.000306* | *0.000370* | *0.000447* |
| 10 | *0.000537* | *0.000645* | *0.000773* | *0.000922* | *0.00110* |
| 20 | *0.00131* | *0.00155* | *0.00183* | *0.00216* | *0.00254* |
| 30 | *0.00299* | *0.00350* | *0.00410* | *0.00478* | *0.00558* |
| 40 | *0.00648* | *0.00752* | *0.00872* | *0.01008* | *0.01163* |
| 50 | *0.01340* | *0.01541* | *0.01768* | *0.02027* | *0.02319* |
| 60 | *0.02648* | *0.03020* | *0.03439* | *0.03909* | *0.04437* |
| 70 | *0.05029* | *0.05692* | *0.06432* | *0.07258* | *0.08179* |
| 80 | *0.09204* | *0.1034* | *0.1161* | *0.1301* | *0.1457* |
| 90 | *0.1628* | *0.1818* | *0.2028* | *0.2259* | *0.2513* |
| 100 | *0.2793* | *0.3100* | *0.3438* | *0.3807* | *0.4212* |
| 110 | *0.4655* | *0.5140* | *0.5668* | *0.6245* | *0.6873* |
| 120 | *0.7557* | *0.8301* | *0.9109* | *0.9987* | *1.094* |
| 130 | *1.197* | *1.309* | *1.430* | *1.560* | *1.701* |
| 140 | *1.854* | *2.018* | *2.195* | *2.385* | *2.59* |
| 150 | *2.811* | *3.047* | *3.302* | *3.574* | *3.866* |
| 160 | *4.179* | *4.514* | *4.873* | *5.256* | *5.665* |
| 170 | *6.102* | *6.568* | *7.065* | *7.594* | *8.158* |
| 180 | *8.758* | *9.396* | *10.07* | *10.79* | *11.56* |
| 190 | *12.37* | *13.23* | *14.15* | *15.11* | *16.14* |
| 200 | *17.22* | *18.36* | *19.58* | *20.86* | *22.21* |
| 210 | *23.63* | *25.14* | *26.72* | *28.40* | *30.16* |
| 220 | *32.01* | *33.96* | *36.02* | *38.18* | *40.45* |
| 230 | *42.83* | *45.34* | *47.96* | *50.72* | *53.62* |
| 240 | *56.64* | *59.82* | *63.15* | *66.64* | *70.29* |
| 250 | *74.10* | *78.09* | 82.27 | 86.63 | 91.19 |
| 260 | 95.94 | 100.91 | 106.09 | 111.50 | 117.14 |
| 270 | 123.02 | 129.14 | 135.52 | 142.17 | 149.09 |
| 280 | 156.29 | 163.78 | 171.57 | 179.66 | 188.08 |
| 290 | 196.81 | 205.92 | 215.31 | 225.14 | 235.31 |
| 300 | 245.85 | 256.79 | 268.13 | 279.89 | 292.07 |
| 310 | 304.69 | 317.77 | 331.30 | 345.32 | 359.82 |
| 320 | 374.82 | 390.34 | 406.39 | 422.97 | 440.13 |
| 330 | 457.85 | 476.20 | 495.06 | 514.59 | 534.74 |
| 340 | 555.54 | 576.99 | 599.13 | 621.97 | 645.57 |
| 350 | 669.77 | 694.78 | 720.56 | 747.11 | 774.45 |
| 360 | 802.62 | 831.60 | 861.44 | 892.15 | 923.75 |
| 370 | 956.25 | 989.68 | 1024.0 | 1059.4 | 1095.7 |
| 380 | 1133.0 | 1171.4 | 1210.7 | 1251.2 | 1292.8 |
| 390 | 1335.4 | 1379.2 | 1424.1 | 1470.2 | 1517.6 |
| 400 | 1566.1 | 1615.8 | 1666.9 | 1719.2 | 1772.9 |
| 410 | 1827.5 | 1884.1 | 1941.8 | 2000.9 | 2061.4 |
| 420 | 2123.4 | 2186.9 | 2251.9 | 2318.3 | 2386.4 |
| 430 | 2456.0 | 2527.3 | 2600.1 | 2674.7 | 2753.6 |
| 440 | 2828.8 | 2908.5 | 2990.0 | 3073.1 | 3158.2 |
| 450 | 3245.0 | *3333.8* | *3424.5* | *3517.1* | *3611.7* |

## STUDIES IN VAPOR PRESSURE: III. A DYNAMIC METHOD FOR MEASURING VAPOR PRESSURES, WITH ITS APPLICATION TO BENZENE AND AMMONIUM CHLORIDE.

For high vapor pressures, to the measurement of which a vessel closed with a rubber stopper is unsuitable, a modified form of the submerged bulblet apparatus[1] may be used. The new apparatus is less easily constructed, but, when made, has several advantages, for all purposes, over the simpler form. To avoid repetition, we mention only the few points in which the new apparatus differs from the old, and refer the reader for all further description and directions, and for a discussion of the theory and characteristics of the method, to the former papers. This instrument, to distinguish it from the static apparatus described in a preceding paper, will be called the "dynamic isoteniscope."

### THE EXPERIMENTAL METHOD.

**The Apparatus.**—The opening *C* (Fig. 1) is connected with the gage, the exit to the air, and the pressure (or vacuum) bottle and pump.[2] The bulb *B* (diameter 23 mm.) contains the liquid through which the stream of vapor is discharged. The bulblet *A* is made as a separate part and, after being charged with the solid or liquid substance under investigation, is fused on to the side tube at the dotted line. When cut apart carefully at this point, after use, the apparatus may be employed repeatedly. The bulb between *A* and *B* prevents access of the liquid in *B* to the bulb *A*. The total length from *B* to *C* is about 30 cm.

The method of manipulation is the same as that described in connection with the submerged-bulblet vapor pressure apparatus.[3]

**Necessary Corrections.**—When the apparatus is employed, the usual precautions and corrections in connection with the gage and thermometer are required. Two corrections are peculiar to this apparatus. One is that for immersed depth, measured in this instance from the surface of the liquid in *B* down to the opening of, or the point of ascension in, the capillary.[4] The second is that due to capillary ascension, which increases the pressure beyond that shown by the gage.[5] The amounts of both corrections may be measured together as follows: After the observations are completed, and the bulb *A* has been cut off, the opening

[1] Submerged bulblet papers: *J. Am. Chem. Soc.*, **32**, 897 and 907.

[2] For general arrangement, see this series, No. I, Fig. 3.

[3] *Loc. cit.*

[4] *J. Am. Chem. Soc.*, **32**, 901.

[5] *Ibid.*, **32**, 902.

*C* is connected with a wide tube standing in a beaker of water. The latter tube is raised, drawing its water content with it until the surface of the confining liquid in *B* falls to the point of ascension, or until bubbles issue from the capillary, as the case may require. The elevation of the water above the surface in the open beaker gives the value in water height of the capillary effect plus the submerged-depth effect. This is reduced to mercury height at 0°, and added to the gage pressure, as usual. The interior of the capillary must be wet with the substance just before the measurement is made. As we have seen, the amount of these corrections is small.

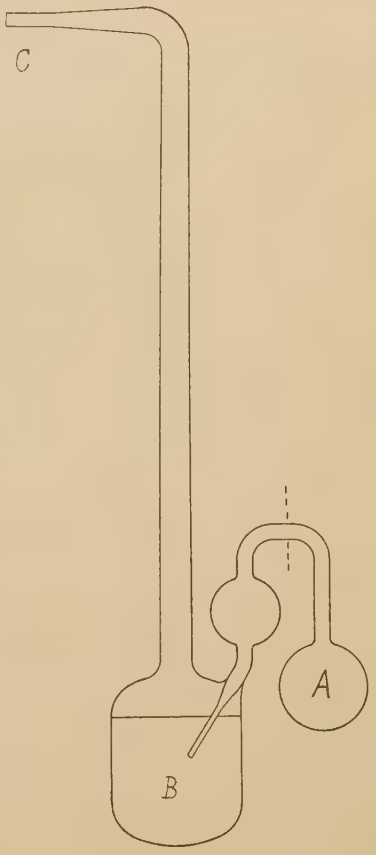

Fig. 1

**Characteristics of this Method.**—The valuable characteristics of the submerged-bulblet apparatus, which have already been described in full are, of course, retained in this dynamic isoteniscope. This form of the apparatus possesses, however, several additional advantages: (1) It can be used for high pressures as well as low. (2) The test tube in the former apparatus contains a large volume of the confining liquid. This acquires the temperature of the outside bath—and therefore transmits it to the bulb of the thermometer—rather slowly. Here the quantity of the confining liquid is much smaller. Then, too, the thermometer is hung directly in the bath liquid and a slight lag in the temperature of the confining liquid in the bulb *B*, if any existed, would have little or no effect upon the vapor pressure values obtained. This arrangement, therefore, permits the making of measurements of equal accuracy more rapidly. (3) The thermometer is not subjected to varying pressures, and the correction for the dilatation[1] of the bulb when the pressures are below 760 mm. is eliminated. Correction for compression of the bulb, due to the immersion in a liquid, may be made, but the magnitude of this correction is very small, averaging only 0.02° for 10 cm. immersion in water.

[1] *J. Am. Chem. Soc.*, **32**, 905.

When compared with the static apparatus, this dynamic apparatus will be seen to retain all the characteristics enumerated when that apparatus was described,[1] and to possess several additional advantages:

(1) There may be difficulty, with the static apparatus, in finding a suitable confining liquid. This difficulty cannot arise when the substance is a liquid, since the substance is employed in the U-tube to confine its own vapor. But when the substance is a solid, no liquid which has an appreciable vapor pressure of its own at the temperatures concerned, and none which interacts with the substance to give a gaseous product, and none in which the vapor of the substance is soluble, may be employed. Cases, such as those of the ammonium halides, phosphorus pentachloride, etc., therefore arise in which suitable confining fluids for certain ranges of temperature are hard to find. Thus, for ammonium chloride, fused silver chloride might be used, but would be available only above its melting point (450–460°). The present dynamic method is much more flexible, since possession of an appreciable vapor pressure by, or miscibility of the substance with, or chemical activity of the substance toward the confining liquid do not usually interfere with the operation of the apparatus, and would not, save in extreme cases, impair the accuracy of the results. The dynamic isoteniscope is therefore applicable to a wider range of cases.

(2) This dynamic method would find application when results by the static and the dynamic methods are to be compared. Such a case is mentioned, for example, by Smits and Scheffer,[2] who give reasons for anticipating that the values of the dissociation pressures of substances like aldehyde-ammonia might be widely different, according as the one or the other method was used.

This method has one disadvantage when compared with the static method, namely, that, in the latter, no corrections for submerged depth or for capillarity are required. The static method is therefore to be preferred, save where use of the dynamic one is indicated by considerations such as those mentioned in the preceding paragraphs.

**The Sample Determinations.**—As we have seen, water is at present the only substance suitable for testing the accuracy of a method of measing vapor pressures. The determinations with this substance, using the simple form of the submerged bulblet, have already shown, however, that an apparatus operating on this principle is capable of yielding results of a high order of accuracy. The present form of the apparatus was applied, therefore, to the measurement of the vapor pressures of benzene and of ammonium chloride.

The bath, stirrer, barometer, gage, and platinum resistance ther-

[1] Studies in Vapor Pressure, I, Sec. 3, *J. Am. Chem. Soc.*, **32**, 1419.

[2] *Z. physik. Chem.*, 65, 70 (1908).

mometer, and the corrections involved in their use, were the same as those employed in the work with the static isoteniscope.[1] It is sufficient here to say that the temperatures are on the thermodynamic scale, assuming the boiling point of sulphur to be 445°, and that the error below 120° (benzene) was ascertained to be less than ±0.01° and above 120° (ammonium chloride) less than ±0.1°.

## THE VAPOR PRESSURES OF BENZENE.

**Determinations by Previous Observers.**—The sample used by Regnault[2] melted at 4.45°, nearly a degree too low, and must have been impure. He employed the dynamic method above 24°. Ramsay and Young[3] removed thiophene and otherwise purified their sample, but do not give the melting point. They used their dynamic method[4] (up to 80°), in which the liquid trickled onto cotton surrounding the bulb of the thermometer. In this instance they state that correction was made for the dilatation of the bulb of the latter *in vacuo*. Young[5] continued the series above 80° by the barometer-static method[6] over mercury, using a part of the original material, and giving temperatures on the scale of the constant-volume air thermometer. Neubeck[7] used purified benzene boiling at 79.9° at 760 mm. The freezing point is not given. He boiled the substance in a flask under reduced pressure. His thermometer was compared with an air thermometer, but he did not correct for dilatation of the bulb *in vacuo*. The values given below are obtained by graphic interpolation from his data. Mangold[8] used benzene from benzoic acid. He gives the melting point 5.5°. He used Schmidt's[9] dynamic apparatus and did not correct for dilatation of the thermometer bulb *in vacuo*. Kahlbaum[10] purified his benzene, but gives no melting point. He determined the boiling points under reduced pressure, admitting air through a capillary, and did not correct for dilatation of the thermometer bulb. Woringer[11] gives no melting point of his purified benzene. He used the static method, over mercury, admitting the substance through a stopcock, but gives no facts in regard to exclusion of dissolved gases. The results found by these six observers are tabulated along with our own below.

[1] *Loc cit.*
[2] *Mem. Acad.*, **26**, 416 (1862).
[3] *Phil. Mag.*, [5] **23**, 61 (1887).
[4] Criticized, this series, No. I, Sec. 2, *J. Am. Chem. Soc.*, **32**, 1418.
[5] *J. Chem. Soc.*, **55**, 486 (1889).
[6] Criticized, this series, No. I, Secs. 1 and 2, *J. Am. Chem. Soc.*, **32**, 1414 and 1416.
[7] *Z. physik. Chem.*, **1**, 649 (1887).
[8] *Sitzungsber. Math.-Nat. Klasse, Kaiserl. Akad.*, **102** (IIa), 1071 (1893).
[9] *Z. physik. Chem.*, **7**, 441.
[10] *Ibid.*, **26**, 600 (1898).
[11] *Ibid* **34**, 262 (1900).

**Purification of the Benzene.**—Kahlbaum's "thiophenfrei," crystallizable benzene was used. It was boiled under reflux with much sodium for three hours, at the end of which time no trace of hydrogen evolution could be detected. It was distilled, and the middle portion of the distillate, amounting to 1.46 liters, was used. This came over, after correction of the temperatures for changes in the barometric pressure, within 0.01°. A portion used for a freezing-point determination was boiled for fifteen minutes to remove dissolved gases. The freezing point was taken by two thermometers, the ice points of which had been ascertained immediately before, and they agreed in giving the value +5.40°.

The physical properties of benzene have been carefully investigated by Lackowitz,[1] who found that they were greatly affected by dissolved air. He showed, for example, that the removal of dissolved air, not considered by previous observers, produced a marked lowering in the specific gravity. His freezing point was 5.42 ± 0.02°. The lower freezing points of previous observers, namely, Regnault 4.45°, Jungfleisch 3.00°, W. Fischer 5.3, and Schoop 5.04, undoubtedly indicate insufficient purification. Linebarger[2] found 5.4° and Mangold 5.5°. Only Flink[3] claims to have reached 6.06°.

It appears, therefore, that our sample was probably as pure as that of Lackowitz. Even if we ignore the possibility, which he admits, that his freezing point may have been 0.02° too high, and assume that ours was lower than his by the same amount, the proportion of impurity which this represents would not noticeably affect the accuracy of the results. At the boiling point (about 80°) it would give an elevation of only 0.01° and lower the vapor pressure by only 0.2 mm. This is the maximum effect reached by assuming that the whole of the supposed impurity was involatil, for our method provides for the removal of dissolved gases during the measurement.

**The Vapor Pressures of Benzene.**—Concentrated sulphuric acid was used as confining liquid in the bulb *B*. Since benzene vapor is soluble in this liquid, the reading was taken when the liquid had ascended the capillary to a fixed mark. Correction was made for submerged depth and for capillarity. The values obtained were as follows:

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| T.. | 63.16 | 66.55 | 71.09 | 74.79 | 80.30 | 90.48 | 95.67 | 100.42 | 105.97 | 111.54 | 119.93 |
| P.. | 439.1 | 492.0 | 563.7 | 640.8 | 765.5 | 1031 | 1197 | 1364 | 1581 | 1820 | 2235 |

The observed pressures were plotted against the temperatures, a smooth curve was drawn through the resulting points, and the value of the pressure every 5° was read off. The results are given in the following table: For comparison, the corresponding values of Regnault (Rg), Ramsay

[1] *Berichte*, **21**, 2210 (1888).
[2] *Am. Chem. J.*, **18**, 437.
[3] *Beibl., Ann. Physik*, **8**, 262.

and Young and Young (Y), Neubeck (N), Mangold (M), Kahlbaum (K), and Woringer (W) are given. The essential details of their methods have been discussed already.

| *t.* | M. | Rg. | Y. | N. | M. | K. | W. |
|---|---|---|---|---|---|---|---|
| 65° | 463 | 463.4 | ... | 465 | 468 | ... | ... |
| 70 | 551 | 547 | 548 | 550 | 554 | 546.5 | 559.5 |
| 75 | 650 | 643 | ... | 645 | 653 | ... | ... |
| 80 | 757.5 | 752 | 755 | 760 | 764.5 | 750 | 773.5 |
| 85 | 879 | ... | ... | ... | ... | ... | ... |
| 90 | 1018 | 1013 | 1008 | ... | ... | ... | ... |
| 95 | 1180 | ... | ... | ... | ... | ... | ... |
| 100 | 1348 | 1340 | 1335 | ... | ... | ... | ... |
| 105 | 1542 | ... | ... | ... | ... | ... | ... |
| 110 | 1751 | 1744 | 1739 | ... | ... | ... | ... |
| 115 | 1983 | .... | ... | ... | ... | ... | ... |
| 120 | 2240 | 2235 | 2230 | ... | ... | ... | ... |

The boiling point, 80.12° at 760 mm., was also read from the curve. The values found by different observers are as follows:

| | | | |
|---|---|---|---|
| Kopp (1847) | 80.40° | Ramsay and Young (1887) | 80.2° |
| Regnault (1863) | 80.36 | Neubeck (1887) | 79.9 |
| Brühl (1880) | 80.08 | Louguinine | 80.20 |
| Flink (1884) | 80.37 | Menzies (1910) | 80.12 |

## THE VAPOR PRESSURES OF AMMONIUM CHLORIDE.

In order further to test the value of the dynamic isoteniscope method of measuring vapor pressures, we sought some substance difficult of study by the older methods. A non-fusing solid, the vapor of which attacked mercury, was required. That comparison might be possible, it was desirable also that the vapor pressures of the substance should have been previously determined by more than one observer and using methods professing some degree of accuracy. Ammonium chloride seemed to be the only such substance. Even with the present exceedingly adaptable method, this salt presented a problem of exceptional difficulty, and the results cannot claim the same degree of accuracy as do those with water and benzene. It will appear, however, that even in this case the limits of accuracy can be stated, and that the results are free from the undefined, and undoubtedly considerable sources of error with which the previous determinations may be charged.

**Previous Determinations.**—The vapor pressures of this salt have been determined by Horstmann,[1] by Ramsay and Young,[2] and by F. M. G. Johnson.[3] Horstmann's method was a dynamic one. He heated ammonium chloride in a combustion tube and noted the readings of a mer-

[1] *Ber.*, **2**, 137 (1869).
[2] *Phil. Trans.*, **177**, 71 (1886).
[3] *Z. physik. Chem.*, **61**, 458 (1908); **65**, 36 (1908).

cury thermometer immersed in the vapor, while the pressure of the air in the tube rose by stages from about 10 mm. to 760 mm.

Ramsay and Young made a large number of observations by several methods. One series from 98° to 280° was obtained statically over mercury in a barometer tube. Some permanent gas accumulated during the observations, and the value at the highest of these temperatures, for example, may be in doubt on this account alone about 0.5° (or 4.5 mm. = 3 per cent. of the whole). Observations from 290° to 340° were secured by enclosing a lump of the salt above a constriction in the closed limb of a U-tube. The bend was filled with mercury, and air pressures of known value could be applied to the vapor of the metal through the open limb. The U-tube was heated by the vapor of mercury boiling under various known pressures, and the corresponding temperatures were taken from Regnault's data, with an error, therefore, of 1° at 340°. Foreign gases and vapors were expelled by lowering the pressure, and allowing the vapor of the salt to escape past the mercury in the U-tube. At 320° and 340° the vapor pressure of the ammonium chloride did not give a constant value, but increased continuously. At 320° this increase was a linear function of the time, but the rate of increase per minute varied in different experiments from 0.2 mm. to 1 mm. per minute. The increase was under observation for as long as 390 minutes in one instance. With the help of time curves, the observations were corrected. This increase is attributed by the authors to the liberation of hydrogen by chemical action of the hydrogen chloride on the mercury. At 340° there was always a very rapid rise in pressure, amounting to from 32 to 67 mm., during the first twenty minutes, before the slower, uniform rise (of from 0.2 to 1 mm. per minute) set in. The authors suggest that the salt was cooled by the immediately preceding, rapid vaporization, and during the twenty minutes was regaining the temperature of the vapor bath. But this effect should have been almost as great at 320°, where no rapid rise was observed. In explaining both of these increases in pressure, the authors ignore entirely the effect of diffusion of the mercury vapor backwards to the surface of the salt. The result of this diffusion must be to increase the pressure and, if complete interdiffusion of the vapors had occurred, the limit would have been reached only when the total pressure equaled the sum of the vapor pressures of ammonium chloride and mercury. The evident fact is that when the confining liquid has a considerable vapor pressure of its own, and the interdiffusion of the vapors is possible during the observation, the resulting measurements of vapor pressure must always be of uncertain value. When we consider the fact that here the vapor pressure of the confining liquid, although less than that of the substance, was of the same order (at 320°, the pressures are 369 mm. and 445 mm., and at 340°, 548 mm. and 760 mm.,

respectively), it is surprising that the readings could be utilized at all.

The same observers made an independent series of measurements by their dynamic method, described in an earlier paper.[1] Here a block of the salt surrounded the thermometer bulb, and the distilling vessel containing the thermometer was heated by means of boiling mercury. The observations were made from 178.5° to 338.9°. The results, when plotted, were found to be somewhat scattered, and all on one side of the rather smooth curve that could be drawn through the points determind by the static method. The pressures at corresponding temperatures are all higher, being at 320° on an average about 56 mm. higher (estimated graphically), at 330° about 80 mm. higher, and at 333.5° about 100 mm. higher. The results by the static and dynamic methods, separately, as well as the values finally adopted, are given in a table at the close of this paper. A supplementary observation by a different dynamic method, in which the mass of the salt surrounding the thermometer bulb was placed in a combustion tube and heated with a Bunsen burner, gave a value at 338.35° of 762.1 mm. This confirmed the results by the static method rather than those by the dynamic, being less than 2° (equivalent to about 35 mm.) below the static temperature at the same pressure, while the dynamic temperature at the same pressure was 6° below static. Hence, the dynamic results were considered to be the less trustworthy, and in the curve which embodies the final results, much greater weight is given the static results. The final data are therefore essentially derived from a static method. The authors state that the difference of less than 2° above mentioned "may well be due to error of experiment." The results at the highest temperature are thus estimated to be subject to an error of at least ±2°, or, according to their curve, ±35 mm. Considering the extreme experimental difficulties involved in the method, this error cannot be considered excessive. The specific sources of error in these methods have already been discussed at length.[2]

F. M. G. Johnson employed the Ladenburg manometer, consisting of a flattened glass tube, wound in a spiral. The external pressure required to bring the attached mirror back to the zero position was measured. His method was therefore static, but he avoided the great difficulties connected with the common static methods in which mercury is used. Assuming that, as the author says, the spiral was capable easily of showing a pressure change of "the order of 1 mm." (although he does not state that this degree of sensitiveness was maintained at 335°), the chief errors to which his method was liable arise from four causes, namely, gases occluded in or absorbed by the solid substance, unequal distribu-

[1] *Phil. Trans.*, **175**, 37 (1886); *J. Chem. Soc.*, **47**, 42 (1885).

[2] This series, No. I, Secs. 1 and 2, *J. Am. Chem. Soc.*, **32**, 1413–9.

tion of temperature in the air bath he used for heating, the untrustworthiness of mercury thermometers at such high temperatures, and the unfortunate method used for standardizing the thermometers. The efficiency of the whole arrangement was, indeed, tested by a determination of the vapor pressures of iodine, and the results were found to agree well with those of Ramsay and Young. But the test ranged from 80.5° to only 178.5°, while the experiments with ammonium chloride ran from 211° to 335°. The temperature errors would not assert themselves strongly until above 200°, so that this test cannot be accepted as a rigid demonstration of the adequacy of the precautions. Attention must therefore be drawn to the sources of error individually.

The apparatus and material were freed thoroughly from moisture by means of phosphorus pentoxide, and to effect this the former was pumped out repeatedly and left evacuated for a long period. The apparatus was heated during the process, for the purpose of assisting the desiccation and of driving out adhering air. But the parts containing the pentoxide and the salt could not be heated. The salt had previously been sublimed twice. It will be seen, however, that the complete expulsion of adhering gases was not insured. The quartz spiral gage used by Preuner and Schupp[1] is so constructed as to permit of boiling out before sealing, when vapor pressures are to be determined. But this process could not be applied when, as was the case with Johnson's apparatus, a bulb for the simultaneous determination of the vapor density was attached. It is a pity that the zero of the gage was not redetermind after the experiments, as this would not only have shown whether any permanent gas had been liberated, but would also have afforded a means of detecting other irregularities, such as a permanent distortion of the spiral.

Johnson's apparatus was heated in an unstirred air bath provided with a gas pressure regulator which kept the temperature constant $\pm 1°$. As we have seen,[2] however, an air bath is by far the least satisfactory means of keeping the temperature uniform and constant. Aside from the inherent causes of defective thermal equilibrium, in this case a copper tube was inserted through the top of the bath, forming a separate compartment surrounding the pocket containing the solid ammonium chloride. The purpose of this was to keep the salt cooler than the bulb and spiral. The temperatures in the copper tube and in the rest of the bath differed by 22° at 323°. Now, if maintaining *one* temperature in an air bath is difficult, keeping *two* temperatures each constant and uniform is much more difficult. This feature of the apparatus, therefore, involves a source of considerable uncertainty.

The temperatures were ascertained with a nitrogen-filled, mercury

[1] *Z. physik. Chem.*, 68, 129.

[2] This series, No. I, Sec. 1, *J. Am. Chem. Soc.*, 32, 1413.

thermometer. It is well known, however, that such a thermometer, when kept for a considerable time at a high temperature, suffers distillation of the mercury into the upper part of the bore,[1] and gives untrustworthy readings, with an error of about $\pm 1°$. On account of the difficulty in making due correction, the error is greater when the thread is not completely immersed.

Finally Johnson standardized the thermometer by using the vapor pressure curve of mercury. The data used were those of Ramsay and Young.[2] Young,[3] however, has himself pointed out and corrected some of the most serious inaccuracies which have meantime come to light in these data. His corrections alter the temperature at 340° by 1°.

The present status of our knowledge of the vapor pressures of ammonium chloride may now be summed up. Horstmann makes no professions of exact thermometry and $\pm 5°$ at the highest temperature is a conservative estimate of the limits of error involved. The known error of Ramsay and Young's measurements is $\pm 1°$ at the lower temperatures and $\pm 2°$ at the highest. But the uncertainty of interpreting the progressive increase in the pressures at 320° and 340° introduces an additional possibility of error, the magnitude of which cannot be assessed. Johnson's measurements are affected by such considerable temperature errors, the most serious of which are of unknown magnitude, that his measurements can be regarded as approximate only. In considering all these determinations, it must be remembered that, at 335°, an error of $\pm 1°$ corresponds to an error of $\pm 15$ mm. in pressure. It is therefore evident that the vapor pressures of ammonium chloride are in need of re-determination by a method which permits of the definite estimation of the limits of error involved.

**The Vapor Pressures of Ammonium Chloride.**—The bulb *A* (outside diameter 22 mm.) was filled completely with ammonium chloride. The latter, Kahlbaum's purest form of the salt, was finely pulverized and was purposely used without drying. Since the method itself involves a fractionation, special treatment to remove volatil impurities was unnecesssary. Hydrochlorides of coal-tar bases were proved to be absent.

The bath was filled with the mixture of potassium and sodium nitrates, and, no other transparent, fusible substance of a suitable nature being available, the outer bulb *B* was charged with the same mixture. The ammonium chloride vapor, in passing through this liquid, caused a continuous production of nitrous oxide. The method was therefore seen

[1] Ostwald-Luther, *Physikochem. Mess*, [1902] 78. In such a thermometer we have frequently observed with a lens droplets of mercury and particles of a red substance (HgO?) accumulating above the thread.

[2] *J. Chem. Soc.*, **49**, 37 (1886). We are indebted to the author for privately informing us of this fact.

[3] *J. Chem. Soc.*, **59**, 629 (1891).

under the greatest disadvantage, since it was impossible to observe a complete cessation of the stream of vapor. The pressure taken was that at which the stream of gas reached a minimum volume.

Our temperature error of less than $\pm 0.1°$ corresponds at the lowest temperature to $\pm 0.25$ mm. and at the highest to $\pm 1.5$ mm. These are therefore the limits of error of the apparatus *per se*. The difficulty in observing the point of minimum gas evolution, however, introduces a special source of error peculiar to this substance. From a consideration of the degree of sharpness with which the observations could be made, we estimate this error at about $\pm 5$ mm. in the individual readings. The consistency of our results, as shown by the way in which they lie upon a smooth pressure-temperature curve, confirms our belief that the errors are not greater than this.

The following results are corrected for immersed depth and for capillarity, and are given to the nearest millimeter:

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Temperature..... | 278.3 | 291.6 | 298.7 | 308.5 | 316.4 | 325.4 | 332.9 |
| Pressure..... | 131 | 199 | 240 | 322 | 406 | 518 | 633 |

For comparison, the data of Horstmann (two points, ×), Ramsay and Young[1] (curve I), Johnson, undried substance[2] (curve II), and those of Menzies (curve III), are plotted in Fig. 2. It will be seen that the last curve lies between the other two.

The following table contains the data read from the various curves. As throwing some light on the relative trustworthiness of Ramsay and Young's static and dynamic methods, as applied to a substance like this, the observations obtained by each of these have been treated separately and the resulting pressure readings are given in two additional columns:

| | | R & Y. | | | | |
|---|---|---|---|---|---|---|
| | | | Observations. | | | |
| *t.* | H. | Curve. | Static. | Dynamic. | J. | M. |
| 280 | ... | 143 | 140.5 | 147 | 132 | 138 |
| 290 | ... | 195.5 | 189 | 200 | 178 | 189 |
| 300 | 259.5 | 264.5 | 251 | 275 | 237 | 252 |
| 310 | ... | 350 | 333.5 | 367 | 309 | 336 |
| 320 | ... | 460.5 | 443.5 | 500 | 401 | 447 |
| 330 | ... | 599.5 | 596 | 675 | 518 | 587 |
| 333.5 | ... | 661 | 653 | 750 | 566 | 642 |
| 340 | 778.1 | 777 | 759.5 | ... | 678 | ... |

From this comparison it will be seen that Ramsay and Young's static results, when taken by themselves, agrees remarkably well with our dy-

[1] Reproduction of the author's own curve. Johnson ignores the curve, which embodies the authors' conclusions from all their observations, and uses for comparison only certain of the single observations, all taken from the static series.

[2] Dr. Johnson informs us that in his first paper (p. 462), the last temperature, 335°, should be 345°. In the curve on the opposite page, the 211° point is misplaced. In the second paper (p. 37), the $NH_4Cl$ curve is incorrect.

namic results, the divergencies exceeding the estimated error of our measurements, namely $\pm 5$ mm., only above 320°. The inferiority of their

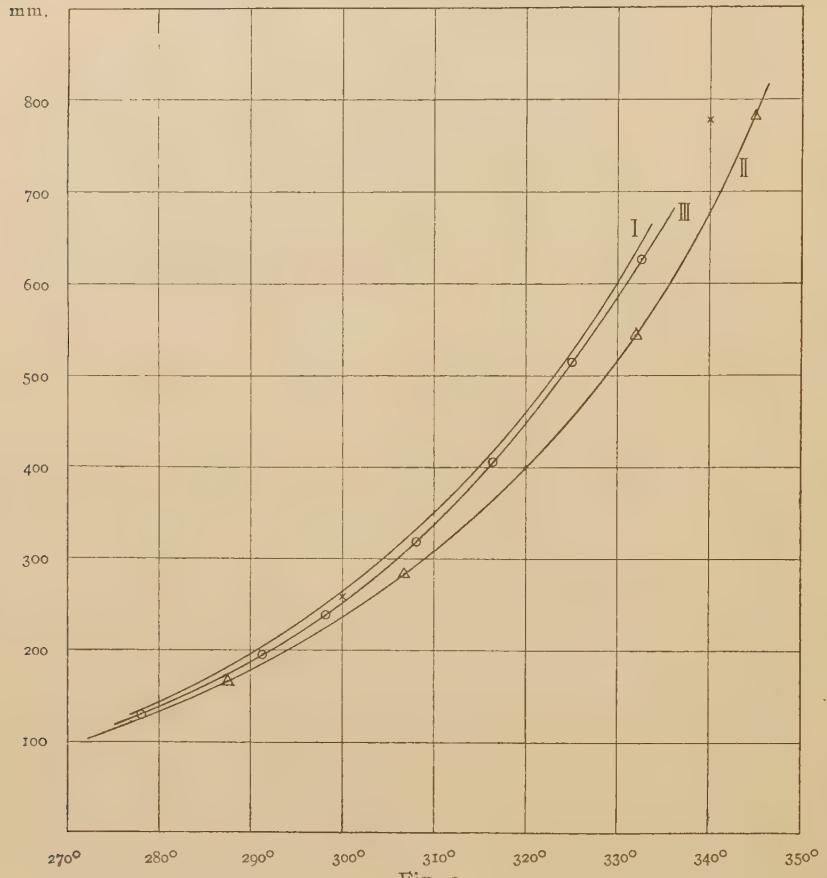


Fig. 2.

dynamic method, at least when applied to a substance like this, is apparent.

## A METHOD FOR DETERMINING THE MOLECULAR WEIGHTS OF DISSOLVED SUBSTANCES BY MEASUREMENT OF LOWERING OF VAPOR PRESSURE.[1]

Among the methods available for measuring the molecular weights of substances in solution, the cryoscopic and the ebullioscopic methods are most commonly used. The method of directly measuring the lowering of vapor pressure due to the dissolved substance has not been commonly applied for molecular weight determination owing, perhaps, to the difficulty of obtaining trustworthy values of vapor pressure by the static method, even when elaborate apparatus is employed. It is proposed in the present paper to describe an apparatus and procedure by means of which, without any thermometer, molecular weights may be simply determind in the laboratory by static measurement of vapor pressure, with an accuracy at least equal to that obtained by the ebullioscopic method.

In 1858 Wüllner,[2] working with aqueous solutions, found the lowering of vapor pressure roughly proportional to the concentration of the dissolved substance. The fact that workers[3] in this field confined their observations to aqueous solution of salts, which are abnormal, prevented the recognition of the underlying regularities until as late as 1886–7. Raoult's work[4] of that epoch is the basis of the present-day cryoscopic and ebullioscopic methods.

Raoult used a barometer tube, static method for measuring vapor pressures of solvent and solution. As with all static methods, chief among the sources of error are (1) the difficulty of completely eliminating gaseous and volatil impurities, and (2) the variation of the superficial concentrations of solutions due to evaporation and condensation. Even were it sufficiently accurate, Raoult's apparatus is too cumbrous for every-day use in molecular weight determination.

[1] Read before the American Chemical Society, Dec. 31, 1909.

[2] *Pogg. Ann.*, **103**, 529 (1858); **105**, 85 (1858); **110**, 564 (1860).

[3] For example, Pauchon, *Compt. rend.*, **89**, 752 (1879); Tammann, *Wied. Ann.*, **24**, 523 (1885); Emden, *Wied. Ann.*, **31**, 145 (1887).

[4] *Compt. rend.*, **103**, 1125 (1886); **104**, 976, 1430 (1887); **107**, 442 (1888); *Z. physik. Chem.*, **2**, 353 (1888); *Ann. chim. phys.*, [6] **15**, 375 (1888).

Air-current or air-bubbling dynamic methods for vapor pressure measurement[1] always appear promising but, perhaps on account of their inflexibility hitherto, they have not come into general use for the purpose under consideration.

After evolving his form of freezing point apparatus, Beckmann[2] turned his attention to devising a workable method of molecular weight determination by vapor pressure measurement. He discarded those methods which he tried, however, in favor of his well-known ebullioscopic method. With the benefit of the experience of these earlier workers, Biddle[3] described a vapor pressure apparatus for molecular weight determination; this, however, is somewhat complex, requires the use of a thermostat, and is applied only to the very volatil solvents, ether and carbon bisulphide.

**The Apparatus.**[4]—As will be seen from Fig. 1, the apparatus here proposed consists of a jacket, in which the solvent is boiled, attached to a small reflux condenser, and an inner "test-tube" furnished with a pressure gage tube and a glass stopper. The dimensions of the jacket are, length 27 cm., diameter 3.5 cm.; those of the inner "test-tube," total length 30 cm., diameter 2.3 cm. The side tube leading from the jacket to the condenser is of glass of 1 cm. bore, so that the solvent may boil under a pressure no greater than barometric. The connection may be made with an 8 cm. length of rubber tubing, furnished with a screw clip. When the glass stopper is removed and the clip closed, the vapor of the liquid boiling in the jacket is obliged to escape by blowing through the gage tube, which is open at both ends, into the test tube. The narrow (6 mm.) U-shaped side tube attached to the jacket returns the cold condensed vapor from the condenser to the lower portion of the jacket, thus avoiding chilling of the upper portion of the test tube. The latter is graduated in cubic centimeters from 15 cc. upwards, and the gage tube (diam. 5 mm.) in millimeters of length (total about 140 mm.) from above

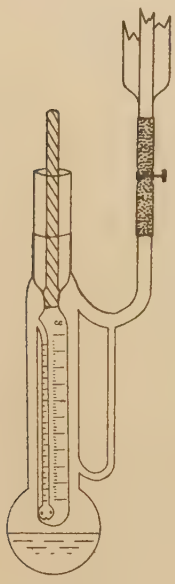

Fig. 1.

[1] Cf. Regnault, *Ann. chim. phys.*, [3] **15**, 129. Tammann, *Wied. Ann.*, **35**, 322. Walker, *Z. physik. Chem.*, **2**, 602. Will and Bredig, *Ber.*, **22**, 1084. Carveth and Fowler, *J. Physic. Chem.*, **8**, 313. Kahlenberg, *Science*, **22**, 74. Earl of Berkeley and Hartley, *Proc. Roy. Soc. London*, **77**, 156. Perman, *Proc. Roy. Soc., London*, **72**, 72. Lincoln and Klein, *J. Physic. Chem.*, **11**, 318. Krauskopf, *Ibid.*, **14**, 489.

[2] *Z. physik. Chem.*, **4**, 532.

[3] *Am. Chem. J.*, **29**, 341.

[4] This may be had from the Central Scientific Co., 349 W. Michigan Street, Chicago, Ill.

downwards. The two sets of graduations are readable from aspects at right angles to each other, so as to avoid confusion. At its foot, the gage tube is blown into a small bulb in which are pierced a number of holes to distribute the vapor as it issues. A glass stopper, with a glass-rod handle (length 12 cm.), fits the constricted neck (diam. 12 mm.) of the test tube, while the test tube itself fits into its jacket by a ground joint. The purpose of the jacket is to maintain the test tube and its contents at a constant temperature—the boiling point of the solvent—while the purpose of the test tube is to contain the solution whose vapor pressure is being measured. The pressure measurment is made in terms of the difference of level of the solution in the gage tube and the test tube, that is, in terms of millimeters of a liquid of low density compared to mercury. Differences of pressure that are small in terms of millimeters of mercury may therefore be measured with accuracy, and this permits of the use of very dilute solutions.

**The Procedure.**—The procedure followed in making a molecular weight determination may properly be described in some detail. The bulb of the jacket is charged two-thirds full with the pure solvent, the empty "test tube" replaced in position, and the liquid boiled with a small naked flame for ten minutes under its reflux condenser, in order to expel dissolved gases. The flame is then removed, the test tube taken out and charged two-thirds full with the boiled-out liquid from the jacket and replaced in position with its stopper left out. The liquid in the jacket is again boiled for a minute to expel air, after which the screw-clip is closed sufficiently to cause a vigorous bubbling of vapor through the liquid in the test tube. After this "blowing-through" process has continued two or three minutes, the stopper is warmed up by inserting it obliquely in position. Vapor can still escape, but the condensed liquid collects to form several drops above the stopper. When this has taken place, the stopper is pushed home, the liquid above it serving to make the joint gas-tight, and at the same moment the screw clip is fully opened. At this stage, the temperature of the liquid in the test tube is slighly higher than the boiling point, because the liquid in the jacket has been boiling under a slightly increased pressure in order to cause the "blowing-through." The apparatus must therefore be allowed to stand for a few minutes until the temperature of the vapor chamber adjusts itself to the true boiling point of the solvent. As the jacket is clamped loosely only at its neck, the apparatus may be shaken occasionally with a jerking motion, by way of stirring.

If the dissolved gases have been removed, and if the solvent is perfectly pure and dry, the relative levels of the liquid in the test tube and gage tube will now be precisely the same as they were before the stopper was inserted; unless the solvent has been very carefully purified, how-

ever, such theoretical perfection will not be quite attained. It is obvious that the liquid in the gage tube stands somewhat the higher of the two, on account of capillarity, as shown in Fig. 2 (*a*). This reading of difference of level is taken as the zero reading, and affords an excellent test of the adequate purity of the solvent. Should the zero reading be unsatisfactory, the process of blowing-through may be repeated until at least constant results are obtained. All readings are conveniently made with the help of a small lens.

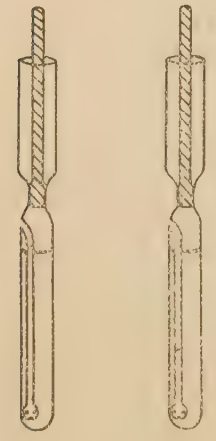

Fig. 2.

On removing the stopper, the substance may now be introduced in the form of weighed pastils, or otherwise. Solution is assisted by a gentle "blowing-through," which is necessary also to remove air. When the liquid is judged to be homogeneous and air-free, the stopper is again inserted, exactly as before, and the apparatus allowed to stand with shaking every half minute or so. At this stage the shaking, which should jerk the solution so as to wash the upper portion of the vapor-chamber walls, is very essential if surface films of abnormal concentration are to be avoided. By the circulation it causes, shaking also hastens the cooling of the central portions of the solution to the boiling point of the pure solvent. At no time, of course, must the boiling of the pure solvent in the jacket be interrupted. In about ten minutes, when the difference of level (see Fig. 2 (*b*)) after successive shakings has become constant, the reading is made and corrected by the zero reading.[1] The stopper is now removed and the volume of the solution read off, the liquid above the stopper being first removed by filter paper.

Further measurements may be made at different concentrations, either by adding more solute or else by blowing through for some time and so adding more pure solvent. Such further measurements are, however, usually unnecessary, since, with the very dilute solutions employed, the values first obtained are hardly improved by the method of extrapolation to infinit dilution.

In the case of solvents as volatil as carbon disulphide, a common test-tube filled with cold water may be inserted in the projecting upper portion of the "test tube" during the blowing-through process, if necessary to assist condensation. If, for any solvent, the rubber connection is considered objectionable, a glass stopcock[2] of large bore may take the place of the screw clip, and the use of rubber be entirely avoided.

[1] If the apparatus be allowed to stand over a couple of minutes without shaking a slow change of level appears, caused by distillation within the vapor chamber towards the stopper.

[2] To regulate more easily the passage of small quantities of vapor, notches should be filed at the sides of the holes piercing the stopper of the cock.

**Calculation of Results.**—From the well-known relationship

$$p - p' = P\sigma/(\rho - \sigma)$$

where, at any temperature, $p$ is the vapor pressure of the pure solvent, $p'$ that of the solution, $P$ the osmotic pressure of the solution, $\rho$ its density and $\sigma$ the density of the vapor under the pressure[1] $p$, one may, in the case of very dilute solutions, by assuming van't Hoff's law and making the appropriate substitutions for $P$ and $\sigma$, deduce for a barometric height of 760 mm.:

$$p - p'(\text{in mm. mercury}) = n \cdot m \cdot 760/1000\ (\rho - \sigma)$$

where $n$ is the number of dissolved moles per liter of solution, and $m$ is the molecular weight of the solvent in the gaseous state. In millimeters of solut on partially counterpoised by vapor of density $\sigma$, this would become, if $n = 1$,

$$p - p'\ (\text{in mm. solution}) = m \cdot 760 \cdot 13.59/1000 \cdot (\rho - \sigma)^2$$

where 13.59 is the density of mercury at 0°. By assuming that $\rho - \sigma$ is equal to the density of the pure solvent[2] at its boiling point, one may thus calculate for a series of solvents the values of $K_{760} = p - p' =$ the lowering of vapor pressure in mm. of boiling solvent that would be caused by the presence of one mole of non-volatil solute in one liter of solution, the barometer being normal. The values of $K_{760}$ for some of the common solvents are as follows:

| Solvent. | Density at boiling point. | $K_{760}$. |
|---|---|---|
| Benzene | 0.8149 | 1214 |
| Alcohol | 0.7389 | 871.5 |
| Water | 0.9587 | 202.5 |
| Chloroform | 1.4101 | 620.4 |
| Acetone | 0.7518 | 1061 |
| Ether | 0.6968 | 1577 |
| Carbon disulphide | 1.2223 | 526.6 |
| Ethyl acetate | 0.8302 | 1320 |
| Ethylene dibromide | 1.9423 | 514.6 |

If desired, the actual value for $\rho$ for any solution may be found directly by making a weighing of the test tube and its contents, in addition to reading off the volume of the solution, and $\sigma$ may be calculated. This, however, is unnecessary for the ordinary purposes of molecular weight determination, and was not done in the examples given below.

[1] Should $p - \frac{p - p'}{2}$ be preferred, since with this apparatus $p - p'$ has values from about 3 to 7 mm. of mercury, the constants $K$ would become from one-quarter to one-half per cent. smaller.

[2] At their boiling points under 760 mm., $\sigma$ for carbon bisulphide, benzene, chloroform and alcohol has a value about 0.24, 0.33, 0.31 and 0.32 per cent., respectively, of $\rho$. If the densities of the solutions used in this apparatus exceeded the density of the pure solvent by precisely these amounts, no error would be committed by the assumption made.

The change of $\rho$ due to a change of boiling point of the solvent caused by a barometric divergence of 10 mm. from the normal is of the order of 1 part in 1000, and is therefore negligible.

Knowing the value of $K_{760}$ as given above, the molecular weight may be calculated from the formula

$$M = 1000\, W \cdot K \cdot B / L \cdot V \cdot 760$$

where $W$ is the weight of solute added, $L$ is the measured lowering of pressure in mm., $V$ is the volume of the solution in cc., and $B$ is the barometric height.

**Examples of Results.**—The table below gives examples of the results obtained with six solvents. The benzene was the crystallizable, thiophene-free product of Kahlbaum and was dried and distilled over sodium. The carbon disulphide was distilled once. The alcohol, also Kahlbaum's, was dried and distilled over barium oxide. The chloroform was freed from alcohol by washing with chromic acid mixture and dried over calcium chloride. A quantity of acetone, from the bisulphite compound, was distilled once with a Hempel's fractionating tube, and the first portion of the distillate taken. The solutes were also the preparations of Kahlbaum, and were used without further purification other than drying. In the table, the results of Beckmann[1] and of Walker and Lumsden[2] are added for comparison. The figures refer to the lowest and the highest concentrations which they used:

| Weight of solute. | Volume of solution. | Lowering observed. | Molecular weight found. | Beckmann found. | W. & L. found. |
|---|---|---|---|---|---|
| | | *Solvent, Water.* | | | |
| | | Potassium Nitrate, 101. | | | |
| 0.611 | 36.7 | 57.1 | 56.9 | | 53 |
| 0.611 | 37.7 | 56.9 | 57.0 | | |
| 0.611 | 38.2 | 56.4 | 56.6 | | |
| | | Sodium Chloride, 58.5. | | | |
| 0.351 | 38.0 | 56.2 | 32.5 | | 32 |
| 0.579 | 40.4 | 84.4 | 33.3 | | |
| 0.488 | 33.8 | 84.4 | 33.4 | | |
| | | *Solvent, Benzene.* | | | |
| | | Naphthalene, 128. | | | |
| 0.3115 | 48.1 | 60.1 | 128.6 | 141–144 | 139–141 |
| 0.5118 | 49.1 | 105.2 | 127.5 | | |
| 0.3237 | 46.1 | 65.2 | 128.0 | | |
| 0.5092 | 46.8 | 101.6 | 127.3 | | |
| | | Anthracene, 178. | | | |
| 0.336 | 45.0 | 48.5 | 186.2 | 192 | 184–187 |

[1] *Z. physik. Chem.*, **6**, 437.
[2] *J. Chem. Soc.*, **73**, 502.

| Weight of solute. | Volume of solution. | Lowering observed. | Molecular weight found. | Beckmann found. | W. & L. found. |
|---|---|---|---|---|---|
| | | *Solvent, Carbon Disulphide.* | | | |
| | | Naphthalene, 128. | | | |
| 0.4166 | 43.2 | 32.2 | 126.3 | 131–141 | |
| 0.7632 | 43.8 | 69.6 | 128.6 | | |
| 1.0386 | 44.3 | 95.7 | 125.9 | | |
| | | Anthracene, 178. | | | |
| 0.8504 | 44.7 | 55.0 | 178.2 | 175–185 | |
| 1.4255 | 46.5 | 90.8 | 173.9 | | |
| 1.8503 | 51.0 | 109.0 | 171.4 | | |
| | | *Solvent, Alcohol.* | | | |
| | | Naphthalene, 128. | | | |
| 0.425 | 37.0 | 64.1 | 153.7 | 148–155 | 147–157 |
| | | Mercuric Chloride, 271. | | | |
| 1.058 | 42.0 | 83.0 | 260.2 | 263–271 | 261–263 |
| | | *Solvent, Chloroform.* | | | |
| | | Naphthalene, 128. | | | |
| 0.447 | 43.1 | 47.5 | 133.4 | 128–133 | 125–126 |
| 0.865 | 43.5 | 93.6 | 129.9 | | |
| 0.804 | 44.7 | 81.5 | 136.0 | | |
| | | *Solvent, Acetone.* | | | |
| | | Naphthalene, 128. | | | |
| 0.3264 | 41.9 | 60.4 | 133.2 | 128–155 | |
| 0.3424 | 39.6 | 68.6 | 131.8 | | |
| 0.3424 | 39.7 | 68.6 | 131.9 | | |
| 0.4874 | 40.8 | 92.2 | 133.5 | | |

For the following determinations I am indebted to Mr. Severin Gertken, who was without previous experience of molecular weight determination by any method:

| Weight of solute. | Volume of solution. | Lowering observed. | Molecular weight found. | Beckmann found. | W. & L. found. |
|---|---|---|---|---|---|
| | | *Solvent, Carbon Disulphide.* | | | |
| | | Benzil, 210. | | | |
| 1.851 | 47.4 | 98.9 | 206.5 | 217 | |
| | | Benzophenone, 182. | | | |
| 1.069 | 47.2 | 59.6 | 195.9 | 182–187 | |
| 1.069 | 47.3 | 59.7 | 196.3 | | |
| | | Naphthalene, 128. | | | |
| 0.988 | 51.6 | 77.4 | 127.6 | 131–141 | |
| | | *Solvent, Benzene.* | | | |
| | | Benzil, 210. | | | |
| 0.650 | 50.3 | 26.1 | 203.0 | 216–256 | |
| | | Ethyl Benzoate, 150. | | | |
| 0.662 | 53.2 | 90.5 | 164.5 | 163–172 | |

| Weight of solute. | Volume of solution. | Lowering observed. | Molecular weight found. | Beckamann found. | W. L. found. |
|---|---|---|---|---|---|
| | | *Solvent, Water.* | | | |
| | | Boric Acid, 62. | | | |
| 1.201 | 43.0 | 90.7 | 61.6 | 64.6–66.9 | |
| 1 147 | 46.7 | 79.2 | 62.1 | | |
| 1.147 | 46.3 | 81.2 | 61.4 | | |
| | | Potassium Chloride, 74.6. | | | |
| 1.001 | 44.8 | 102.2 | 44.2 | | |
| 1.001 | 45.0 | 103.1 | 43.2 | | |
| 1.001 | 45.2 | 102.4 | 43.3 | | |

In the values found for the molecular weight, the first decimal place has been retained for purposes of comparison, but it is of little value.

**Comparison with Ebullioscopic Methods.**—That this method possesses greater potentialities for accuracy than the ebullioscopic method will be admitted when it is considered that an elevation of boiling point of 0.1° corresponds to a measured lowering of vapor pressure of, for example, 37, 55 and 37 mm., respectively, for water, alcohol and benzene. It should therefore be possible, with like accuracy, to employ. with this method, much more dilute solutions. This leads to the consideration of a chief source of error of the ebullioscopic methods when the more dilute solutions are employed, namely, change of boiling point due to change of barometric pressure during the experiment. To cause an error of temperature of 0.05°—fifty per cent. of the quantity measured in the case above considered—the barometer need change only 1.36 mm., 1.5 mm. and 1.2 mm., respectively, for water, alcohol and benzene. Such barometric changes affect the results of the method here described scarcely at all, since the temperature of the jacket varies proportionally, and thus automatically corrects this error. Change of barometer influences the result only by slightly affecting the constant $K$, which depends on absolute barometric height, as indicated above. It may be pointed out that, in the case of the ebullioscopic methods, the constant used is customarily obtained experimentally and not by calculation from theory as in the case of the method here outlined.

The time occupied in a first determination by this method may be thirty to forty minutes, including the necessary weighing. In discussing the Beckmann boiling point method, H. Biltz[1] states that 'it usually requires one hour, but often two, and sometimes, indeed, several hours, to obtain a constant temperature in the boiling vessel.' How much of this trouble is due to slow change of zero of the thermometer is difficult to say. Presumably very little, as the Landsberger type of apparatus is much more expeditious, in the form, for example, devised by McCoy.[2]

[1] "Pract. Methods for Determining Molecular Weights," Transl. by Jones and King, p. 155.

[2] See *Am. Chem. J.*, **23**, 357 (1900).

Apropos of the thermometer, it will be recalled that a Beckmann thermometer whose degree is correct at zero is 3.6 per cent. in error[1] at 100°. Accordingly, whenever a Beckmann thermometer is employed at temperatures far from that at which its degree is correct, a correction for this error becomes necessary, although it is frequently omitted. The absence of any thermometer in the present apparatus simplifies slightly the reading of the volume of the solution; when a thermometer is pres nt, it must first be removed.

In this apparatus, the 1 cc. graduations have a distance apart of about 2.8 mm., which makes the estimation of tenths satisfactory.

A considerable error is incident to both Berkmann and Landsberger methods when the correction for varying head of liquid above the thermometer bulb is neglected. Such an error does not here appear, for it is on the measurement of precisely such heads of liquid that the present method is based.

The use of a reflux condenser avoids the errors caused by change of temperature due to fractionation of the jacketing liquid inherent in the Landsberger method and its modifications.

**The Identity of Vapor Pressure as Determined by the Static and by the Dynamic Methods.**—It was tacitly assumed above that the statically determind vapor pressure of a pure liquid at its boiling point, determind dynamically, should be precisely the pressure under which the liquid boiled. In other words, it was taken for granted that if $p$ is measured statically for any particular $t$, the same $t$ will be arrived at dynamically by a boiling point measurement if $p$ be the same. As is well known, however, it was by no means always agreed that this is the case.[2]

The apparatus here described is well adapted for testing the facts. The vapor pressure of the pure solvent in the test tube is a "static" vapor pressure, and is measured at the dynamically attained temperature of the vapor from the pure solvent boiling in the jacket. The pressure comparison is made by a differential gage of a liquid of low specific gravity, instead of, for example, by the difference of level of two mercury columns, one of which has a small depth of another liquid lying on its surface. With benzene, for instance, a pressure difference of 0.5 mm. of mercury, obtained in other methods by subtraction of much larger numbers of mm. and the application of not a few corrections, is, by this method, seen directly on a single small apparatus as a difference of level of 8.3 mm. of benzene at its boiling point (which is the manometer liquid). More important than simplicity of the pressure reading, however, is the possibility of boiling out dissolved gases until constant results are ob-

[1] *Z. Instrum.*, 1896, 202.

[2] References to the extensive literature of the controversy on this subject may be found in Ostwald's *Lehrbuch*, Vol. I, 308.

tained; because failure to realize this possibility has been a chief cause of inconsistences in all measurements by the static method.

As, therefore, it seemed of interest to determin whether any small difference could be detected between static and dynamic results, the experiment was made with pure water, alcohol and benzene. The following figures refer to benzene, which had recently been distilled over sodium, but was not boiled out in the jacket. The differences of pressure, $\Delta p$, are in mm. of benzene at its boiling point, while the times, $T$, refer to the number of minutes of the "blowing-through" process:

| | | | | | |
|---|---|---|---|---|---|
| $\Delta p$ | 6.3 | 2.5 | 0.9 | 0.1 | 0.1 |
| $T$ | 5.0 | 6.0 | 8.0 | 10.0 | 12.0 |

The zero reading was that found when the stopper was removed. It will be seen that the difference of pressure finally observed was not larger than the limits of the error of observation.

It was shown in a similar way that, if any difference exists between the vapor pressure at the boiling point as measured dynamically and statically of the liquids water and alcohol, then such difference does not exceed 0.01 mm. of mercury.

**Purpose and Scope.**—In the present paper, the purpose has been to describe a molecular weight apparatus and its every-day application in cases where the greatest refinement is not aimed at. When opportunity offers, it is proposed to carry the measurements to their highest accuracy, and to make such applications of the method as promise to be most productive.

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## A CONVENIENT FORM OF APPARATUS FOR THE MEASUREMENT OF THE VAPOR DENSITIES OF EASILY VOLATIL SUBSTANCES.[1]

By the very slight modification here explained, the apparatus described in the preceding paper may be simply adapted for the rapid and accurate measurement of vapor densities of easily volatil substances.

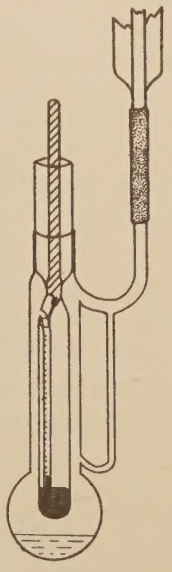
The principle employed is that of the measurement of the increase of pressure that occurs when a known weight of substance is introduced into a closed vessel at constant temperature, high enough to completely volatilize the substance.[2]

**The Modification Required.**—The closed chamber is provided by

[1] Read before the American Chemical Society, July 15, 1910.

[2] For other work in this field cf. Gibson Dyson, *Chem. News*, **55**, 88 (1887); Bleier and Kohn, *Monatsh.*, **20**, 909; **21**, 575; Lumsden, *J. Chem. Soc.*, **83**, 342; Blackman, *Chem. News*, **100**, 13; etc.

the "test-tube" of the former apparatus, which is the inner tube in the figure. This is closed below by pouring in from six to eight cc. of mercury. This mercury serves at the same time the purpose of manometer liquid, indicating by its rise in the graduated narrow gage tube the increase of pressure within the test tube.



The substance is weighed off in bulblets whose attached capillaries, 2–3 cm. in length, are sealed off before the final weighing. In order to attach the bulblet to the stopper of the test tube, the latter must be provided with a hole of about 1.5 mm. diameter and 5–6 mm. length. This hole may be drilled in the glass stopper, or else *added* by fusing to the lower end of the stopper a short length of thick-walled tubing of 1.5 mm. bore. The point of the bulblet's capillary can now be fixed in this hole by stuffing with a few shreds of dry asbestos. The hole should be oblique, in order that the neck of the bulblet may be broken by rotating the stopper in such a way that the bulblet is forced against the top of the gage tube (see figure). It is evident that the presence of this small hole in no wise unfits the apparatus[1] for its original purpose.

**The Procedure.**—The bulb of the outer jacket is charged one-third full with a liquid of suitably high boiling point, which is caused to boil steadily, the vapor thus serving to jacket the whole of the closed portion of the test tube. It is most convenient in practice to find a constant for the apparatus, at the temperature used, by volatilizing a known weight of a standard liquid, such as benzene, rather than to calculate the vapor density from measurements of the volume of the closed chamber and of the temperature. A quantity of benzene suitable to give a rise of mercury level of about 100 mm. is, therefore, sealed and weighed in a bulblet. The smaller the bulblet that will hold the requisite quantity of liquid, the better. The neck of the bulblet is then prepared for easy breaking by one or two scratches from a file. The tip of the capillary is inserted in the hole in the stopper, and the latter, after suitable lubrication, placed cautiously in its position. As the air surrounding the cold bulblet becomes warmed, the mercury rises a few mm. in the gage tube and in 5–6 minutes has reached a constant level, which is read off on the engraved scale of mm. Its position is shown in the figure. The stopper is now rotated so as to snap the neck of the bulblet, which falls on to the surface of the mercury. At the same instant the mercury in the gage

[1] The apparatus, with the modified stopper, may be had from the Central Scientific Co., 349 W. Michigan Street, Chicago, Ill.

tube shoots up, and reaches a constant level in a few seconds. The amount of rise is observed, and is corrected by adding the amount of the simultaneous slight fall of mercury level in the test tube.[1] From the three data (1) weight of benzene taken, (2) known molecular weight of benzene, (3) rise in mm., is calculated a constant for the apparatus, $K$, which is the rise in mm. that would be caused by the volatilization of one gram-molecular weight of any substance in this apparatus at this temperature. Having obtained this constant, the unknown molecular weight of any substance may be calculated by substituting the measured rise, $R$, and weight taken, $W$, in the formula

$$M = W \cdot K/R.$$

After each measurement, the stopper is removed and a current of air aspirated through the test tube for a few seconds by introducing into it the end of a tube connected with the water pump. Several of the broken bulblets may be allowed to accumulate in the apparatus.

**Examples of Results.**—The measurements recorded below, including the time necessary for the weighings and for finding the constant of the apparatus, were completed in a period of three hours. The jacket contained boiling toluene. The substances whose molecular weights are determined were the preparations of Kahlbaum, each dried and purified by distillation. The chloroform was previously freed from alcohol by washing with chromic acid mixture. Every result obtained is given:

| Substance. | Weight taken. | Rise in mm. | Log. $K$. | Molecular weight. Found. | Molecular weight. Normal. |
|---|---|---|---|---|---|
| Benzene..... | 0.0238 | 16.5 | 5.5820 | .... | 78.05 |
| | 0.0205 | 100.5 | 5.5827 | .... | .... |
| Ethyl iodide..... | 0.0429 | 104.7 | 5.5824 | 156.7 | 156.0 |
| | 0.0328 | 80.5 | .... | 155.8 | .... |
| Carbon disulphide.. | 0.0262 | 132.1 | .... | 75.8 | 76.1 |
| | 0.0180 | 90.7 | .... | 75.9 | .... |
| Chloroform..... | 0.0312 | 99.9 | .... | 119.4 | 119.4 |
| | 0.0347 | 110.0 | .... | 120.6 | .... |
| Methyl iodide ..... | 0.0328 | 87.4 | .... | 143.6 | 141.9 |

For the following determinations, I am indebted to Mr. R. D. Mullinix, who was without previous experience of vapor density measurements by any method, and who, indeed, first learned to weigh accurately in order to make these determinations. The jacket contained commercial xylene, b. p. 137.8°. Every determination made by Mr. Mullinix, other than his preliminary ones, is recorded:

[1] The value of this correction for a given rise of mercury in the gage tube having been determined once, the values for other cases are thereafter obtained by simple proportion.

| Substance. | Weight taken. | Rise in mm. | Log. $K$. | Molecular weight. Found. | Molecular weight. Normal. |
|---|---|---|---|---|---|
| Benzene..... | 0.0215 | 112.0 | 5.6091 | ... | 78.05 |
| | 0.0210 | 110.3 | 5.6126 | ... | ... |
| | 0.0211 | 110.1 | 5.6098 | ... | ... |
| Toluene..... | 0.0246 | 110.2 | 5.6105 | 91.1 | 92.1 |
| | 0.0231 | 100.2 | .... | 93.2 | |
| | 0.0248 | 108.0 | .... | 93.6 | |
| Acetone..... | 0.0158 | 108.1 | .... | 59.6 | 58.0 |
| | 0.0157 | 108.9 | .... | 58.9 | ... |
| | 0.0156 | 113.8 | .... | 55.9 | ... |
| Chlorobenzene..... | 0.0276 | 100.1 | .... | 112.4 | 112.5 |
| | 0.0270 | 95.5 | .... | 115.3 | ... |
| | 0.0266 | 89.1 | .... | 121.8[1] | ... |
| Ethyl iodide..... | 0.0418 | 108.6 | .... | 157.0 | 156.0 |
| | 0.0409 | 107.1 | .... | 155.7 | ... |
| | 0.0433 | not completed—stopper leaked | | | ... |
| Pyridine..... | 0.0216 | 108.9 | .... | 80.9 | 79.0 |
| | 0.0238 | 124.0 | .... | 78.2 | ... |
| | 0.0233 | 120.7 | .... | 78.5 | ... |
| Acetic acid[2]..... | 0.0140 | 92.6 | .... | 61.7 | 60.0 |
| | 0.0162 | 106.7 | .... | 61.9 | |

As an example of the application of this apparatus to a special problem, the percentage composition of a binary mixture of substances of known molecular weight may be found. For this purpose, the solubility of carbon disulphide in methyl alcohol was determined at 22.2°. The average molecular weight of the upper layer obtained on mixing these liquids was found to be 52.5, which would give a percentage of carbon disulphide of 53.4. Interpolation from the data of Rothmund[3] would lead to 52.3. In cases of this kind, other analytical methods are sometimes troublesome.

**Remarks on the Method.**—The apparatus is considerably more compact than the Victor Meyer form, and stands at a convenient level above the working bench. It is very simply set up, requiring a single ring stand with two clamps, one of which holds the condenser.

If a constant be determined as suggested, correction is, of course, not necessary for the density of mercury or for its vapor pressure. If a record be kept of the volume of mercury employed, the constant need not be redetermined when the apparatus is next used.

[1] At normal pressure, chlorobenzene boils at 132°. The temperature of the jacket was 137.8°. As the pressure within the closed chamber increases, the volatilization of the chlorobenzene from the bulblet becomes rather slow.

[2] It will be seen that the values obtained for acetic acid, whose vapor is known to be associated, differ little from the monomolecular value. It must be recalled that, in this apparatus, the partial pressure of acetic acid vapor in the closed chamber is less than one-seventh of an atmosphere.

[3] *Z. physik. Chem.*, 26, 475.

Correction for change of jacket temperature due to barometric change is negligible. Thus, 23 mm. change of barometer causes a change of 1° in the boiling point of toluene (384° absolute), or 1 part in 384 in the result.

When the final level of the mercury in the gage tube is very different from that measured in finding the constant of the apparatus, it is plain that the gas content of the test tube will be somewhat different. Correction for this is usually unnecessary, and was not made in the above examples.

As every portion of the enclosed chamber is kept at the constant high temperature, there is nothing to be feared from the diffusion of the vapor to colder parts of the apparatus, as in the case of the Lumsden or Victor Meyer apparatus. Thus, Lumsden remarks:[1] "The accuracy of the results depends very much on the rapidity with which the substance is vaporized, and this is the more important the smaller the molecular weight, since a vapor which diffuses rapidly may reach the colder part of the apparatus before a measurement of pressure can be made." Again, as no air is driven from a hotter to a colder place, no uncertain correction on this account has to be considered.[2]

Since the vapor is likely to be diffused throughout the whole of the test tube, and since the pressure read is less than one-sixth of an atmosphere, the partial pressure of the vapor cannot even locally much exceed one-sixth of an atmosphere. This low pressure lessens any tendency to association, as is seen in the acetic acid example given above. It is obvious that the test tube may be filled with an inert gas if desired.

Instead of a glass stopper, a one-holed rubber cork may be used at the lower temperatures. A glass rod, bent for the lowest centimeter of its length, passes through the hole, and by its timely rotation breaks the neck of the bulblet, which is inserted into a small blind hole beside it, and is pressed against the top of the gage tube. This form of "release" is perhaps easier to operate than that described above.

In the form described, this apparatus is not suitable for temperatures above 200°; but the examples given seem to show that it is both rapid and accurate for use at temperatures at which it is applicable.

In carrying out the work of this dissertation, I have been throughout constantly indebted to the suggestion and counsel of Prof. Alex. Smith, to whom I wish to express my very best thanks.

[1] *Loc. cit.*

[2] Cf. T. W. Richards, *Chem. News*, 59, 87.